

分析化学手册

FENXIHUAXUESHOUCE

第七分册

核磁共振波谱分析



化学工业出版社
CHEMICAL INDUSTRY PRESS

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（第二版）

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核磁共振波谱分析

于德泉　杨峻山　主编

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第二版前言

分析化学是人们获得物质化学组成和结构信息的科学。由于多学科的交叉渗透，现代分析化学已发展成为一个庞大的学科体系，建立起了比较成熟的多种分析方法，包括色谱分析、电化学分析、光谱分析、波谱分析、质谱分析、化学分析、热分析、放射分析、生化分析等。它一方面在科学研究中起着至关重要的作用，极大地推动着其他学科的发展；另一方面还直接服务于国民经济和生产建设的需要。同时，当代科学技术和人类生产活动的飞速发展也向分析化学学科提出了严峻的挑战，并带来了前所未有的发展机会。

我国的分析化学学科在新中国建立以来，特别是改革开放以后，取得了长足的发展。到目前为止，在全国范围内已形成了一支以中国科学院和高等院校及各部委研究所为核心的分析化学科研队伍，和一个涉及生物、环境、材料、临床、医药、地质、冶金、石化、宇航、商检、法医、侦破和考古等领域的庞大分析检验队伍，共同构成了我国分析化学学科研究发展的源泉和推广应用的基地。在多年的发展过程中，无论是分析化学的基础理论，还是实际应用方面，都已形成了丰富的知识和经验的积累，需要进一步的总结和推广。

《分析化学手册》是一部比较全面的反映现代分析技术，供化学工作者使用的专业工具套书。手册第一版自 1979 年出版以来，在读者中形成了一定的影响，已成为许多分析化验室的必备图书。但由于受组稿时的历史条件所限，加上近 20 年来是世界和我国的科学技术，包括分析化学学科飞速发展的时期，原手册第一版在内容和编排上已不能全面反映当前我国分析化学的发展现状。因此，根据广大读者的要求，我们组织了这套《分析化学手册》的修订工作。

在第一版原有 6 个分册的基础上，这次经扩充和修订为以下 10 个分册：

第一分册　基础知识与安全知识

第二分册　化学分析

第三分册　光谱分析

第四分册　电分析化学

第五分册　气相色谱分析

第六分册　液相色谱分析

第七分册　核磁共振波谱分析

第八分册　热分析

第九分册　质谱分析

第十分册　化学计量学

其中第一分册为基础内容，收集了分析工作中常用的基础数据、分析实验

室的安全知识及分析数据的常规处理、计算机应用的基础知识。第十分册所涉及的化学计量学是近些年来发展非常迅速的化学学科的一个分支，与分析化学有着特殊密切的关系，它应用数学和统计学的方法，并引入计算机科学的发展成果，其研究对象几乎涉及分析化学的所有过程，对于设计或选择最优的分析方法，解析大量的化学分析数据以最大限度地获取化学信息等具有普遍的指导意义，因此修订时增加这一部分内容。其他各分册均是按分析方法及所采用的主要仪器类型来划分，大体包括两方面的内容：基础原理、基础数据部分和实际应用部分。

本次修订，在内容上我们着重收录了基础性的理论和发展较为成熟的方法及应用，注意推陈出新，更新有关数据，增补各自领域近些年的新发展新成果，特别是计算机应用、多种分析手段联用技术的发展，以及分析技术应用于生命科学等的内容。

在编排方式上，进一步突出了手册的可查性。各册均编排主题词索引，与目录相互补充。手册中所涉及的名词术语统一采用国家自然科学名词审定委员会发布的标准，计量单位参照国家标准《GB 3100～3102—93·量和单位》的有关规定贯彻执行。其他凡有国家标准的也一律采用相关最新标准。

第二版的重编修订工作得到了我国分析化学界的大力支持，包括11位中国科学院院士在内的近30位知名专家、学者应邀担任了手册修订的编委会成员，全套书的修订出版凝聚着他们大量的心血和期望，在此谨向他们，以及在编写过程中曾给予我们热情支持与帮助的有关院校、科研单位及厂矿企业的专家和同行们，致以衷心的感谢。同时我们也真诚地期待着广大读者的热情关注和批评指正。

《分析化学手册》编委会

1996年6月

本分册修订说明

本分册在第一版《分析化学手册》中作为第五分册出版至今已有10年左右，在此期间核磁共振波谱技术得到迅速发展，进人近代核磁共振谱时期，其特点是方法学千变万化，而其基本参数，基本原理则维持不变，即化学位移和偶合常数两大参数，对测定化学结构仍显示巨大威力。

在^{1}H及^{13}C核磁共振谱所能提供的数据中，最重要的是化学位移，其中^{1}H谱的偶合常数也很重要。对于不少的亚结构，已有成熟的经验公式可以进行估算。但对于较复杂的结构，尤其是多环体系，则仍需与相近的已知结构对比才能说明问题。这些数据往往散见于文献中。查阅文献时如果碰到的对照化合物近似程度不够高，则有可能得出错误的结论，因而有一本比较完备的手册很有必要，本手册即为此目的而设。

但一本手册没有可能把浩如烟海的文献数据都汇集起来，必须有所侧重，力求在代表性与特殊性之间达成合理的仲裁。通过近年来本手册原有版本的应用情况，对手册内容进行了一些必要的增删，其中主要是删去了颇占篇幅的黄酮^{1}H谱图，适当吸收了一些新数据，对工业产品有所照顾。这样可以进一步扩大手册的应用面。

本分册由三部分（三篇）内容构成：第一部分是有关核磁共振波谱的基本原理、重要谱学方法和有关参数的定义、概念等基础知识与理论；鉴于在第一版中基础知识方面的内容过于精炼，不能适应NMR技术飞速发展的形势，在修订版中增补为第一篇“核磁共振波谱的基本学理，重要谱学方法和有关参数……”，以补充原版的不足。第二部分是各类有机化合物的结构与^{1}H核磁共振的化学位移、偶合常数数据；在这部分中，删去了原第一版中一些不重要的图表，如黄酮类化合物等，而增加一些更具代表性结构的^{1}HNMR数据，同时在选材方面充分考虑各类化合物的用途。第三部分是各类有机化合物的结构与^{13}C核磁共振的化学位移，在每一章的开头增加了一些概念性的结论，供读者参考。书中还适当介绍了^{15}N、^{19}F、^{31}P等核的化学位移，介绍了多维核磁共振方法。本书末尾的目录列出一些比较重要的有关NMR术语的缩写及英汉对照。

本书中注意贯彻了国家标准GB《量和单位》的基本原则，注重所用单位及符号与有关的标准规定的一致性。例如，长期以来化学位移（δ）一直是以ppm作为单位，本次修订依据国际纯化学与应用化学联合会（IUPAC）1982年关于δ的定义，将其单位改为1（即去掉数字后的ppm）。

本书为从事核磁共振的技术人员及从事有机结构研究工作的人员提供了多种类型大量化合物（特别是天然有机化合物）的丰富、翔实的数据资料。上面已指出^{1}H及^{13}C的规律性（取代基加和性经验公式）还是很强的，读者往往可以比较精确地估计出类似结构的预期数值。其结果是在应用过程中能动地扩大了手册资料的实际收载量。因此可以预期，本手册的新版将在有机化合物结构鉴定工作中发挥良好的作用，成为得力的参考工具。

在这次修订过程中，我们认真听取各方意见，力求新版更充实实用。在编写修订大纲过程中得到梁晓天院士、王敬尊教授等有关专家的大力支持和指导，并提出许多宝贵意见，

在此致以衷心感谢。但由于编者水平所限，书中缺点错误之处在所难免，欢迎读者批评指正。

编者

1999年1月于北京

内 容 提 要

第二版《分析化学手册》在第一版的基础上做了较大幅度的调整、增删和补充。全套书由10个分册构成：基础知识与安全知识、化学分析、光谱分析、电分析化学、气相色谱分析、液相色谱分析、核磁共振波谱分析、热分析、质谱分析和化学计量学。

第二版《分析化学手册》中注意贯彻了国家标准GB《量和单位》的基本原则，注重所用单位与有关国际规定的一致性。在取材上突出实用性，注重基础知识、基础数据与分析技术的最新进展并容。在内容上注重科学性与准确性。在编排上强调系统性与查阅方便。

本分册由三部分（三篇）内容构成：第一部分是有关核磁共振波谱的基本原理、重要谱学方法和有关参数的定义、概念等基础知识与理论；第二部分是各类有机化合物的结构与^{1}H核磁共振的化学位移、偶合常数数据；第三部分是各类有机化合物的结构与^{13}C核磁共振的化学位移数据。书中还适当介绍了^{15}N、^{19}F、^{31}P等核的化学位移，介绍了多维核磁共振方法。

本书为从事核磁共振分析工作的人员及从事有机结构研究工作的人员提供了大量化合物（特别是天然有机化合物）的丰富、翔实的数据资料。

目　　录

第一篇　核磁共振谱的基本原理、重要谱学方法及参数

第二篇 质子核磁共振谱的化学位移和偶合常数

第三篇 ^{13}C 核磁共振谱的化学位移和偶合常数

表 目 录

第一篇　核磁共振谱的基本原理、重要谱学方法及参数

第一章　核磁共振的物理基础

1946年美国期坦福大学和哈佛大学的F.Bloch和E.M.Purcell两个研究组首次独立观察到核磁共振信号，为此他们两人荣获1952年诺贝尔物理奖。自此以后，核磁共振谱学快速发展而成为化学家、生物化学家、物理学家以及医学家的不可缺少的物理方法。在1980年以前核磁共振谱主要采用一维谱图，即只有一个频率坐标，而第二个坐标为信号强度。80年代以后，二维核磁共振谱发展成熟被常规使用，即二个坐标轴皆为频率坐标，而信号强度出现在第三维空间。近几年又发展成功三维或多维核磁。当然，三维或多维核磁技术目前尚未达到常规使用的阶段。二维核磁共振谱的发明是核磁共振技术划时代的发展，在二维核磁共振谱方面做出突出贡献的瑞士核磁共振谱学家R.R.Ernst获得1991年诺贝尔化学奖。

核磁共振谱在化学中主要是用来测定分子的化学结构，尤其是天然存在的复杂有机分子结构。从液体核磁共振谱中可得到多方面的结构信息，而这些信息用其他方法是难以得到的。核磁共振谱多在液体中测定。固体核磁共振谱则是完全不同的实验技术，而且谱图的解释也是相当复杂的。

所有自旋量子数不等于零的原子核理论上皆能产生核磁共振信号。但是在有机分子研究中，通常测定核磁共振信号的原子核主要为^{1}H和^{13}C，另外^{19}F、^{31}P、^{15}N等核的核磁共振谱在一些领域也常被采用。要理解核磁共振谱，必须首先了解，自旋的原子核在外磁场中的行为。下面简单介绍核磁共振的物理基础以及重要的光谱参数[1~4]。

第一节　核角动量和核磁矩

原子核由于自旋，从而使其具有核角动量（$\boldsymbol{P}$）和磁矩（$\boldsymbol{\mu}$），角动量是量子化的，可用（1-1）式表示：

$$\boldsymbol{P}=\sqrt{I(I+1)}\hbar \qquad (1\text{-}1)$$

此处，$\hbar=h/2\pi$，h是Planck常量（6.6256×10^{-34}J·s）。I是自旋量子数，通称核自旋。核自旋有以下值，$I=0$，1/2，1，3/2，2…6（见表1-1）。角动量（$\boldsymbol{P}$）与磁矩（$\boldsymbol{\mu}$）有关。两者为矢量，互成正比如下：

$$\boldsymbol{\mu}=\gamma P \qquad (1\text{-}2)$$

γ是一个常数，称为核磁旋比，每种核具有不同的γ值，它决定核在核磁共振实验中检测的灵敏度，γ值大的核，检测的灵敏度高，即共振信号易被观察，反之γ值小的核则是不灵敏的。

将上述（1-1）式和（1-2）式合并则磁矩（$\boldsymbol{\mu}$）如（1-3）式所示

$$\boldsymbol{\mu}=\gamma\sqrt{I(I+1)}\hbar \qquad (1\text{-}3)$$

核自旋为0的核不具磁矩，因此不产生核磁共振信号，例如^{12}C和^{16}O。

表 1-1 在核磁共振谱学中若干重要原子核的性质

原子核	核自旋 (I)	电四极矩 [eQ] [$10^{-28}m^2$]	天然丰度/ %	相对灵敏度①	磁旋比 $\gamma[10^7T^{-1}s^{-1}]$	核磁共振频率/ MHz ($H_0=2.3488T$)
^{1}H	1/2	—	99.985	1.00	26.7519	100.00
^{2}H	1	2.87×10^{-3}	0.015	9.65×10^{-3}	4.1066	15.351
^{3}H②	1/2	—	—	1.21	28.5350	106.664
^{6}Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	—	98.9	—	—	—
^{13}C	1/2	—	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	—	0.37	1.04×10^{-3}	−2.7126	10.133
^{16}O	0	—	99.96	—	—	—
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	−3.6280	13.557
^{19}F	1/2	—	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	−1.6389	6.1195
^{29}Si	1/2	—	4.70	7.84×10^{-3}	−5.3190	19.865
^{31}P	1/2	—	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	−1.8028	6.728
^{57}Fe	1/2	—	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	—	8.58	5.18×10^{-2}	−10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	—	33.8	9.94×10^{-3}	5.8383	21.499

① 相对灵敏度指恒定外磁场和相等数目核与^{1}H比较。

② ^{3}H是放射性的。

第二节 自旋核在外磁场中的行为

一、自旋核在外磁场中的取向

一个具有角动量$\boldsymbol{P}$和磁矩$\boldsymbol{\mu}$的原子核放在外磁场$\boldsymbol{H_0}$中，其角动量的取向即沿磁场方向的分量$\boldsymbol{P_z}$是整数或半整数，取向的数目决定于磁量子数m，即符合下式：

$$\boldsymbol{P_z}=m\hbar \tag{1-4}$$

m是磁量子数，其值为$m=I$，$I-1$，$I-2\cdots-I$，由此，可清楚看出，角动量和磁矩在外磁场中共有$2I+1$个的值，即共有$2I+1$个取向。对于^{1}H和^{13}C核，其$I=1/2$，所以各有2个取向；而^{2}H和^{14}N，其$I=1$，故各有3个取向（见图1-1）

从式（1-1）和式（1-4）可得到磁矩沿磁场方向z的分量为

$$\boldsymbol{\mu_z}=m\gamma\hbar \tag{1-5}$$

用传统表示法，核磁矩沿外磁场z轴旋进的性质类似于旋转的球体（图1-2）。

旋进频率或拉摩频率ν_L正比于外磁场$\boldsymbol{H_0}$强度

$$\nu_L=\left|\frac{\gamma}{2\pi}\right|\boldsymbol{H_0} \tag{1-6}$$

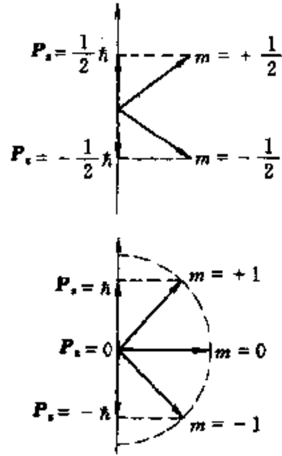


图 1-1 具有 $I=1/2$ 和 1 的核角动量 $\boldsymbol{P}$ 在外磁场中的取向

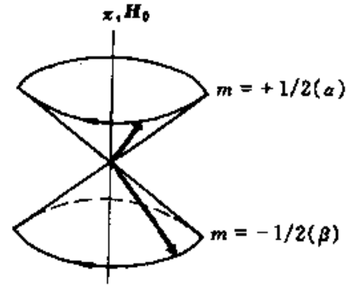


图 1-2 $I=1/2$ 核偶极沿双锥体的旋进锥体的夹角为 54°44′

二、核在外磁场中的能量

核磁矩在外磁场中的能量 E 正比于外磁场 $\boldsymbol{H}_0$ 的强度。从式 1-5 可知，

$$E=-\boldsymbol{\mu}_z\boldsymbol{H}_0 \tag{1-7}$$

此式代入方程式（1-5），则得到方程式（1-8）

$$E=-m\gamma\hbar\boldsymbol{H}_0 \tag{1-8}$$

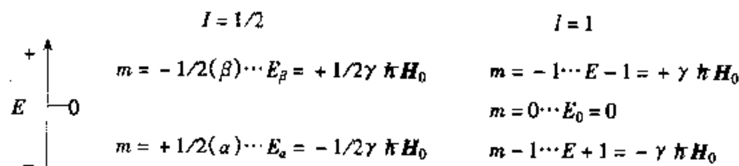


图 1-3 $I=1/2$ 和 $I=1$ 核的能级示意图

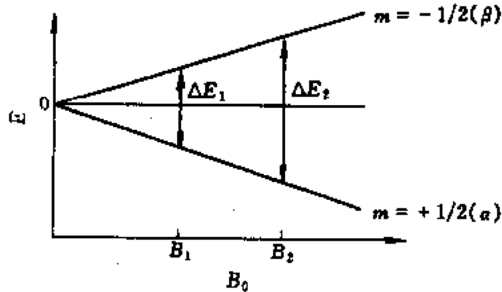


图 1-4 相邻 2 个能级间的能级差与磁场 H_0 的关系

对 $I=1/2$ 的核而言如 ^1H, ^{13}C 等，在磁场中有 2 个取向，即 2 个能级各相应于 $m=+1/2$ 和 $m=-1/2$。假如 $m=+1/2$, $\boldsymbol{\mu}_z$ 平行于 $\boldsymbol{H}_0$ 方向，则 $m=-1/2$, $\boldsymbol{\mu}_z$ 与 $\boldsymbol{H}_0$ 反向。在量子力学中 $m=+1/2$ 能级为自旋态 α，而 $m=-1/2$ 者为自旋态 β。

对 $I=1$ 的核，如 ^2H、^{14}N，在磁场中有 3 个取向，即有 3 个 m 值（+1，0，和 −1），因此有 3 个能级（图 1-3）。

相邻能级间的能级差以式（1-9）所示：

$$\Delta E=\gamma\hbar\boldsymbol{H}_0 \tag{1-9}$$

可见，ΔE 正比于 $\boldsymbol{H}_0$ 的强度，如图 1-4 所示。

三、能级的布居

在热平衡状态下，核在样品管中分布为不同的能级，即处于低能级与高能级，其布居遵守（玻耳兹曼）分配定律，例如 $I=1/2$ 的核，其低能级数日（N_α）与高能级数日（N_β）之比用（1-10）式表示。

$$\frac{N_\beta}{N_\alpha}=e^{-\Delta E/K_B T}\approx 1-\frac{\Delta E}{K_B T}=\frac{\gamma\hbar \boldsymbol{H}_0}{K_B T} \tag{1-10}$$

式中，K_B 为玻耳兹曼常数（$=1.3805\times10^{-23}\mathrm{J\cdot K^{-1}}$）；$T$ 为热力学温度，单位为 K。

对 ^{1}H 及所有其他核，能级差 ΔE 与热运动的 $K_B T$ 相比是非常小的，因此，能级的布居几乎相等。低能级数目略高于高能级，共差别仅为百万分之几通常用 ppm 表示。

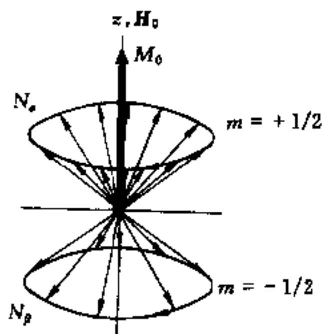


图 1-5 旋进核偶极沿双锥球体的分布

四、宏观磁化量

根据传统表示法，$I=1/2$ 的核（如 ^{1}H, ^{13}C），在双锥球体表面沿外磁场 $\boldsymbol{H}_0 z$ 轴方向旋进（图 1-5）。样品中所有核磁矩沿磁场方向 z 轴的分量称为宏观磁化强度 $\boldsymbol{M}_0$，因为 N_α 略大于 N_β，所以 $\boldsymbol{M}_0$ 代表低能级布居的磁化强度。矢量 $\boldsymbol{M}_0$ 在脉冲核磁共振实验的描述中起到重要的作用。

图 1-5 为旋进核偶极沿双锥球体的分布，图中 $N_\alpha>N_\beta$，故图为组合的宏观磁化强度（$\boldsymbol{M}_0$）。

五、核磁共振条件

在核磁共振实验中，射频作用于样品的核磁矩（偶极），此时如满足式（1-11），

$$h\nu_1=\Delta E \tag{1-11}$$

则低能级核自旋吸收能量，而跃迁至高能级；反之，如高能级核自旋释放出能量，则又恢复为低能级核自旋。两者可能性相等。但由于低能级的布居数多，故从射频中吸收能量是主要过程，从而可观察到共振信号，信号的强度正比于布居差（$N_\alpha-N_\beta$），即正比于样品中低能级核自旋的总数。如果核自旋布居中 $N_\alpha=N_\beta$ 则不呈现共振信号，此时称饱和。

根据式（1-9）和式（1-11）可得到共振条件式（1-12）。

$$\nu_L=\nu_1=\left|\frac{\gamma}{2\pi}\right| \tag{1-12}$$

共振的物理意义在于核自旋的跃迁仅发生于电磁波射频的频率 ν_1 与核自旋拉摩（Larmor）频率 ν_L 的匹配。此时，低能级核自旋吸收射频能量而跃迁至高能级，呈现共振信号。

第二章 核磁共振重要参数、术语和方法[1~4]

第一节 核磁共振的重要参数

一、化学位移

化学位移体现核自旋拉摩频率与其化学环境的关系。拉摩频率是核自旋在外磁场 $\boldsymbol{H}_0$ 中的旋进频率。因为拉摩频率正比于外磁场强度 $\boldsymbol{H}_0$，故无化学位移绝对标度。因此只能采用相对标度，通常采用与标准物比较的方法即测量标准物与被测样品共振频率差。在^{1}H 和^{13}C-NMR 中，多用四甲基硅为内标。为消除不同仪器中外磁场的影响，而采用无因次量 δ，即化学位移，单位是 1❶。

$$\delta = \frac{\nu_S - \nu_R}{\nu_R} \times 10^6$$

在实验操作中，常采用下式

$$\delta = \frac{\nu_S - \nu_R}{\nu_{仪器}} \times 10^6$$

式中 ν_S——试样的共振频率；

ν_R——参比物的共振频率。

二、自旋-自旋偶合

核自旋通过共价键的间接或标量偶合而引起的核磁共振信号裂分为多重峰的现象，在液体核磁共振中而称为自旋-自旋偶合。核自旋通过空间的直接或偶极偶合仅在固态核磁共振中观察到。在液体核磁共振中此种偶合被分子运动所抵消。

三、偶合常数

在多重峰中峰线间的频率差（峰间隔）为偶合常数，单位为 Hz，与化学位移不同，偶合常数不受外磁场强度的影响。偶合常数的大小仅与通过化学键的种类和数目有关。表示方法为：通过一键（^1J 或 J），二键（^2J），三键（^3J，邻位偶合）或四键和五键（^4J,^5J，远程偶合）。例如乙基中 CH_2CH_3，为邻位偶合，$^3J = 7$Hz（图 2-1）。

四、弛豫和弛豫时间

在核磁共振实验中，自旋核的热平衡被射频脉冲的照射所破坏（图 2-2），由此改变自旋核的布居，引起横向磁化分量 M_x 和 M_y。当射频切断，自旋核系统通过弛豫而恢复自旋核布居的玻耳兹曼平衡，横向磁化量 M_y 逐渐减少至零，而纵向磁化量 M_z 则恢复为 M_0，此称弛

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❶ 按 IUPAC 的规定，δ 的单位是 1，也就是说 δ 是个纲量为 1 的量。以前曾经以 ppm 作为单位（现在很多书中也仍在沿用）。

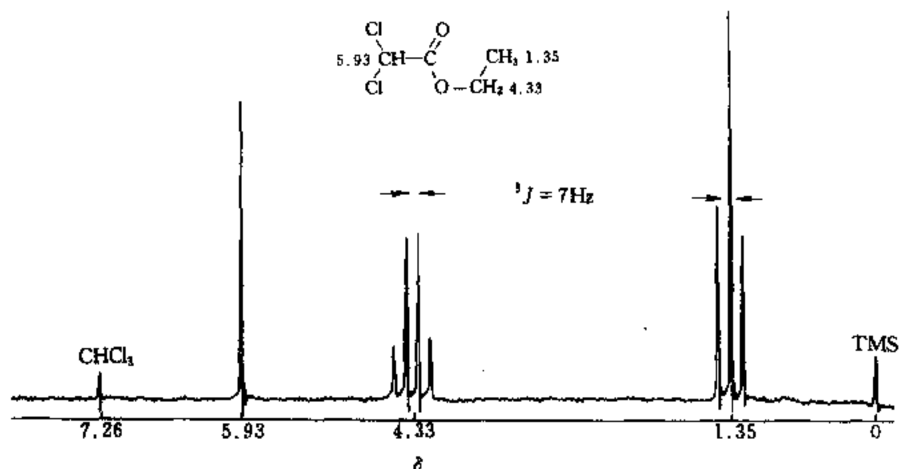


图 2-1 二氯乙酸乙酯^{1}H-NMR 谱（$CDCl_3$，60MHz）
—$CHCl_2$ 的氢与乙酯基中的 CH_2 和 CH_3 比处较低场（比较去屏蔽）

豫过程。弛豫过程有两种，自旋-晶格弛豫和自旋-自旋弛豫。自旋-晶格弛豫发生能量交换，并以指数形式完成玻耳兹曼平衡，能量系通过晶格，即自旋核分子周围的局部波动磁场而改变。自旋-晶格弛豫时间（T_1）是每种自旋核特有的弛豫常数，表明能量交换的效率。T_1 短则弛豫效率高。在 FT-NMR 技术中，T_1 必须与激发脉冲并进。如果脉冲序列太快，例如在^{13}C-NMR 谱中，如脉冲序列快于分子中弛豫最慢 C 原子的 $3T_1$，则弛豫慢的 C 信号强度将减弱。这是由于来不及弛豫的结果。因此，在^{13}C-NMR 谱中季碳信号较弱。

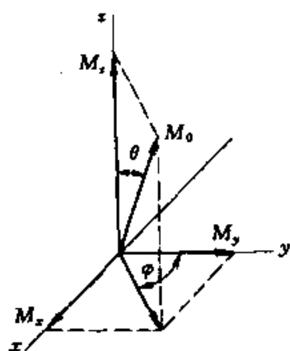


图 2-2 宏观磁化强度 M_0 的 3 个分量 M_x、M_y 和 M_z 在固定坐标系中的分布

自旋-自旋弛豫使横向磁化（即核自旋相干）以指数形式衰减，直至零。FID 衰减的形状可从脉冲 NMR 实验中观察。FID 信号（时间域）经过傅里叶变换则产生 FT-NMR 谱（频率域）。

自旋-自旋弛豫时间（T_2）也是每种自旋核特有的弛豫常数。在溶液中，小分子和中等分子的 T_2 约等于 T_1，自旋核的 T_2 值决定其 NMR 信号的半高宽度，T_2 小则信号宽。分子运动快，则 T_1 和 T_2 值大，信号则尖。此种规则可用于有机化学中最普通的中小分子。化学位移和偶合常数表示分子的静态结构行为，而弛豫时间则反映分子的动力学。

第二节　核磁共振的谱学方法

一、核磁共振信号的多重性

由于自旋-自旋偶合而使核磁共振信号裂分为多重峰称信号多重性。不裂分的信号为单峰（s）。其他多重峰表示为：双峰（d），三重峰（t），四重峰（q），五重峰（qui），六重峰（sxt），七重峰（sep），这种表示法意谓它们的间隔是相同的，即只一个偶合常数，由二个或三个不同偶合常数产生的多重峰，则以二个或三个多重峰表示，如两个双峰（dd），或三裂双峰（ddd）。如果两个双峰的偶合常数均很类似（$J_1 = J_2$），则中间峰重叠，而形成伪三重

峰（t）（见图 2-3）。

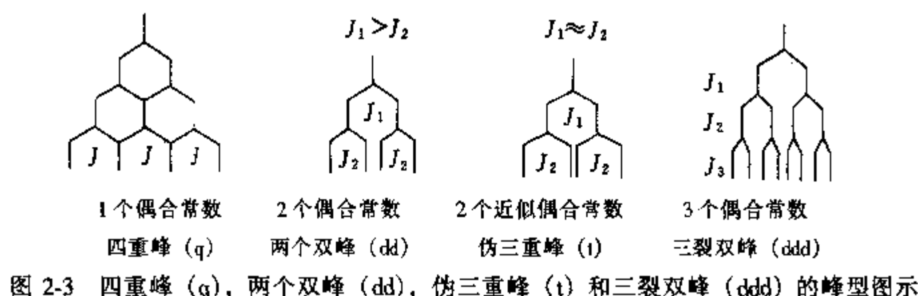


图 2-3 四重峰（q），两个双峰（dd），伪三重峰（t）和三裂双峰（ddd）的峰型图示

二、一级和高级谱图

在偶合体系中，当偶合常数远小于化学位移频率差时，即为一级谱图。此时多重峰的数目符合 $n+1$ 规律，如 A_mX_n 自旋体系，核 A 具有较小的化学位移，而核 X 具有较大的化学位移。一个 AX 系统（图 2-4）系由 A 核双峰与 X 核双峰组成，其间隔为 J_{AX}。

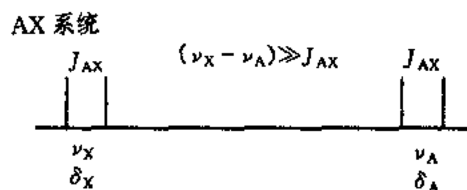


图 2-4 化学位移差远大于偶合常数的 AX 二核自旋体系示意图

适用于一级谱图的多重峰数目规则（如 A_mX_n 系统）：当 n 个 $I=1/2$ 的 X 核与 A 核偶合，则 A 核产生 $n+1$ 个峰。一级谱图中每条线的相对强度遵守 Pascal 三角系数（图 2-5）。

$n=0$ 单峰	1
1 双峰	1 : 1
2 三重峰	1 : 2 : 1
3 四重峰	1 : 3 : 3 : 1
4 五重峰	1 : 4 : 6 : 4 : 1
5 六重峰	1 : 5 : 10 : 10 : 5 : 1
6 七重峰	1 : 6 : 15 : 20 : 15 : 6 : 1

图 2-5 一级谱图中多重峰的相对强度（Pascal 三角）

例如，二氯乙酸乙酯分子中乙基的质子（图 2-1）构成 A_3X_2，其偶合常数 $^3J_{AX}=7Hz$；A 质子具有较小化学位移被裂分为三重峰（2 个邻位质子 X，$n_x+1=3$）；质子 X 呈现四重峰。因为有 3 个邻位 A 质子（$n_A+1=4$）。

由此可见，A 核与 n 个 I_x 核偶合则 A 核多重峰数为 $2nI_x+1$ 条线（图 2-6）。

当一个偶合系统，其化学位移差值与其相应偶合常数值近似，该类系统多重峰数目不符合 $2nI+1$ 规则，此种谱图称高级谱，以 A_mB_n 符号表示，A 核具有较小化学位移，B 核化学位移较大。

例如，一个 AB 系统（图 2-7）由 A 核双峰和 B 核双峰组成，一个偶合常数 J_{AB}，峰型为外边两线低，中间两线高。此种现象称 AB 效应，或称 AB 系统中心“屋顶”对称性，或称向心法则。此种“屋顶”效应在 ^{1}H-NMR 谱中经常可见，即使在一级谱图中，也不例外。在图 2-1 中可见乙基四重峰和三重峰。

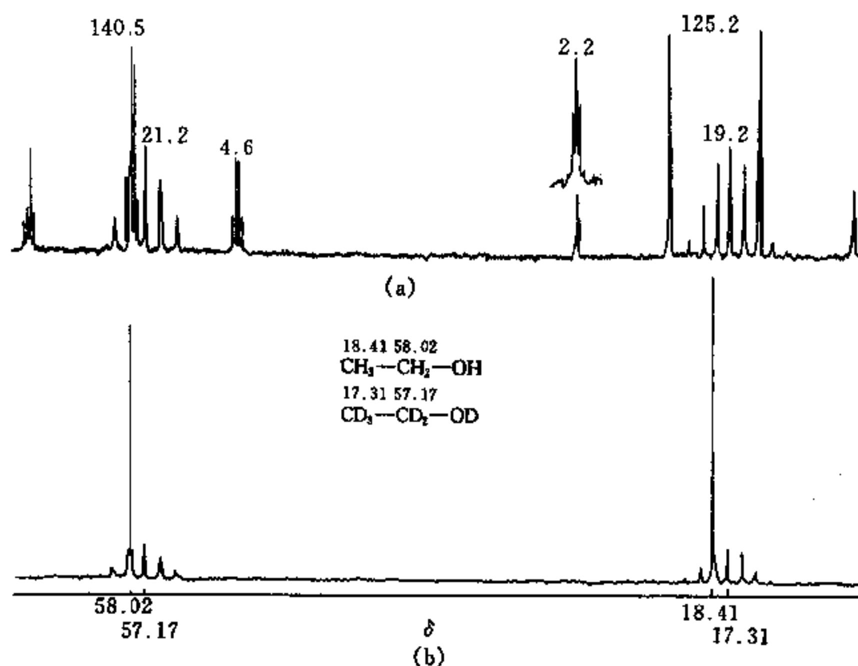


图 2-6 乙醇和六氘代乙醇混合物（27ml + 75ml，25℃，20MHz）的 ^{13}C-NMR 谱
(a) 未去偶谱；(b) 氢宽带去偶谱
对甲基和亚甲基碳的化学位移，氘同位素效应 $\delta_{CH}-\delta_{CD}$ 分别是 1.1ppm 和 0.85ppm

三、化学等价和磁等价

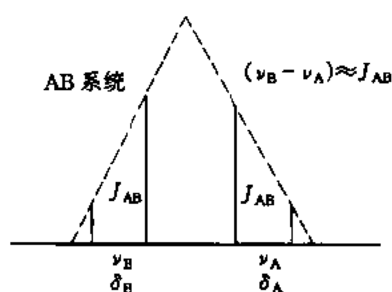


图 2-7 AB 两自旋系统示意图

化学等价 处于相同化学环境的核，称化学等价。化学等价核具有相同化学位移。

例如，1,4-二取代苯分子中的2,2′,3,3′氢，因为分子对称性而化学等价。

磁等价 化学等价的核，如果对其他核发生偶合，而呈现相同的偶合常数，即磁等价。但1,4-二取代苯的2,2′-(A,A′)和3,3′-(X,X′)质子，如 4-硝基苯酚，则非磁等价，因为 A 质子与 X 或 X′质子具有不同的偶合常数。此系统属于 AA′XX′，而不是 A_2X_2 系统。

四、连续波（CW）和 FT 核磁共振谱

测定高分辨 NMR 谱有两种基本的技术。早期用连续波（CW）技术，即在被测定的化学位移范围内采用扫频或扫场方法。通过逐渐增加（或减小）射频而测定图谱，扫描的持续时间长，通常是 2Hz/s，或者 500s 扫 1000Hz，相当于 100MHz ^{1}H 谱中的 10ppm。图 2-1 是 CW 图。

在 FT 技术中，用一个强的射频脉冲在拉摩频率范围短时间激发全部拟观察的核。由此使样品产生横向磁化（M_y），一旦激发停止，则横向磁化 M_y 以指数形式通过 T_2 而衰减。在单自旋情况，NMR 信号是以指数衰减交替电压（自由诱导衰减 FID）形式而记录下来。

在多自旋系统，产生指数衰减交替电压干涉图，即脉冲干涉谱（Pulse interferogram，图

2-8)，每一个交替电压频率是每种核的拉摩频率和激发脉冲频率间的差值。脉冲干频谱通过FT产生拉摩频率谱，即得到所观察核的FT-NMR谱。每个干涉图的FT需时很短，通常低于1s即可完成，这是FT技术的主要优点。在短时间内可积累大量的干涉图并平均化以去噪音，从而可测定低敏核如^{13}C,^{15}N的FT-NMR谱。

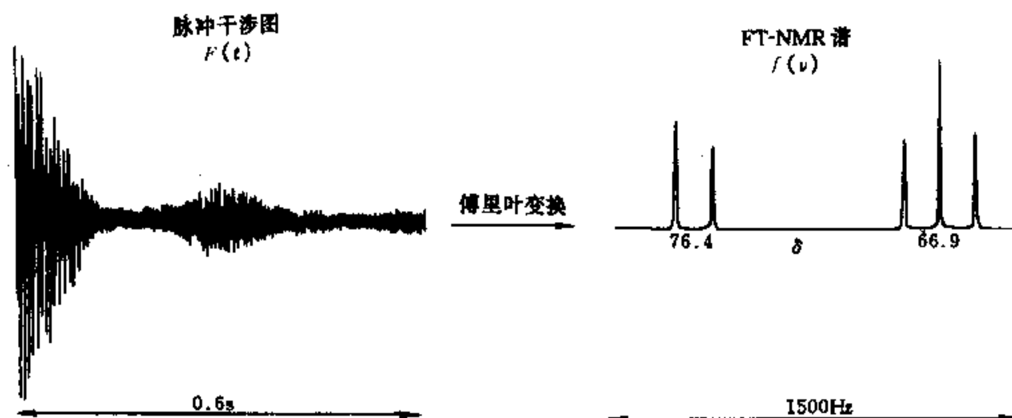


图 2-8 甘油的脉冲干涉谱和FT-^{13}C-NMR谱（D_2O，25℃，100MHz）

五、自旋去偶

自旋去偶（双共振）是NMR的一种技术。最简单例子是AX系统，因为两核互相偶合而各呈双峰。如另用射频在记录全谱的同时而激发A（或X）核，则消除两者的偶合，使之呈现单峰，即发生自旋去偶。如AX为同核，如^{1}H，则称同核去偶。如两者为异核，如^{13}C和^{1}H，则称异核去偶。图2-9为3-氨基丙烯醛的同核去偶。此处为AMX系统[图2-9(c)]，醛基氢X被去偶[图2-9(b)]则简化成AM系统（$^3J_{AM}=12.5$Hz）；如M氢被去偶则简化成AX系

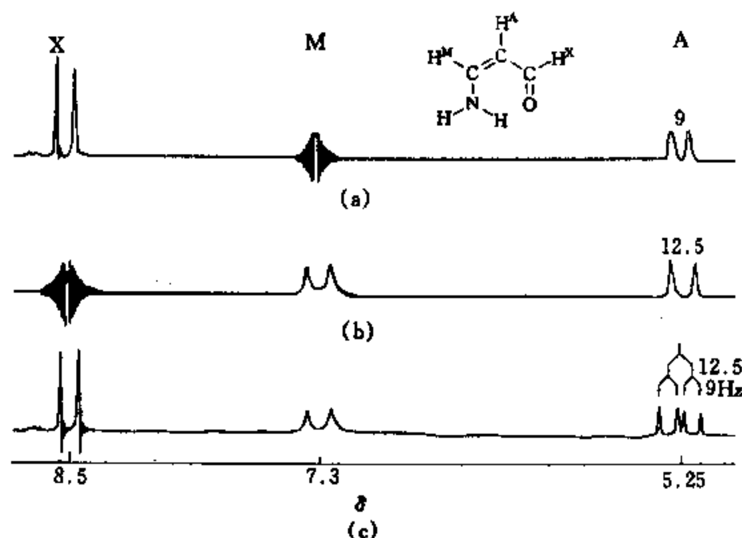


图 2-9 3-氨基丙烯醛CH质子的同核去偶（CD_3OD，25℃，90MHz）
(a) 在$\delta=7.3$去偶；(b) 在$\delta=8.5$去偶；(c) ^{1}H-NMR谱

统（$^3J_{AX}=9Hz$）。由此可说明分子中 H 核间的关系。

在^{13}C-NMR 谱中，常用三种异核去偶。氢宽带去偶，即用一射频在氢核拉摩频率范围照射。产生氢去偶的^{13}C-NMR 谱，每个^{13}C 核呈现一个单峰，称全去偶谱。

图 2-6 为乙醇和六氘乙醇混合物的全去偶^{13}C-NMR 谱。乙醇的 CH_3 和 CH_2 信号，由于氢宽带去偶而分别呈现单峰；而氘代物的 CD_3 和 CD_2 共振峰则分别呈现七重峰和五重峰的精细结构；由于氘核的拉摩频率与氢核不同，氢宽带去偶不影响氘核的偶合，氘核的 $I=1$，根据 $2nI+1$ 的规则，所以 CD，CD_2 和 CD_3 分别为三重峰，五重峰和七重峰。

^{13}C-NMR 的选择性氢去偶谱是通过照射某一特定氢信号而完成的。因此，只有被选择氢去偶的碳信号呈现单峰，其他碳发生偏共振去偶，即 CH 多重峰的每条线靠近，其强度符合 Pascal 三角系数。^{13}C-NMR 选择性氢去偶谱主要用于归属 C—H 键的连接，尤其在 C—H（COSY）技术常规应用之前，该技术用的较多。氢核的偏共振去偶曾用于解决 C—H 多重峰问题，以确定与碳相连的氢的数目。

氢核的脉冲或门控去偶（仅在 FID 间的宽带去偶）可得到偶合的^{13}C-NMR 谱，由于保留 NOE，所以 C—H 多重峰的强度增加，同时并可增加靠近氢核两个键的季碳信号的强度。图 2-10 为2,4,6-三氯嘧啶 C-4 和 C-6 核的门控去偶谱。

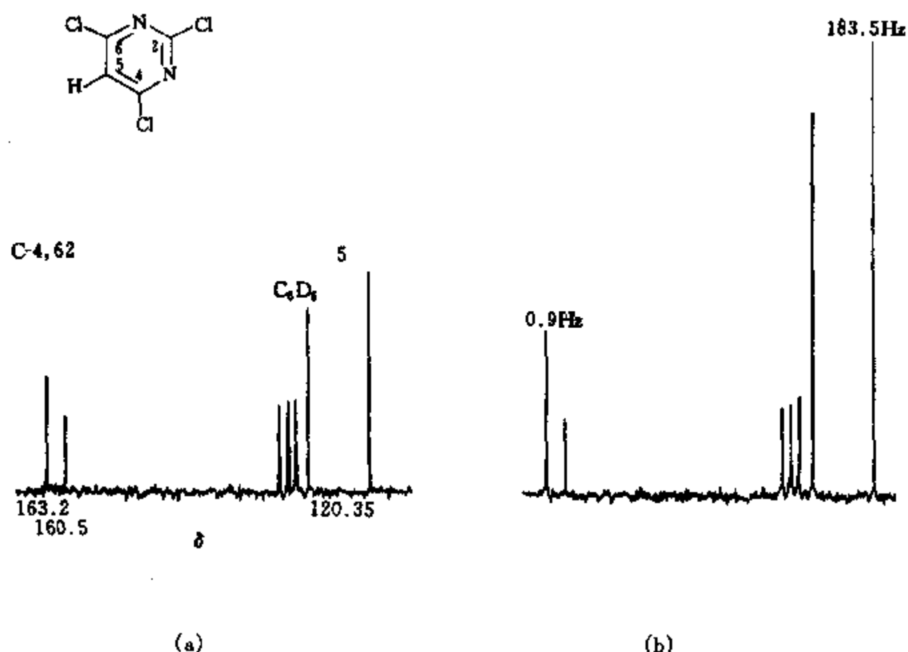


图 2-10　2,4,6-三氯嘧啶的^{13}C-NMR 谱（C_6D_6，25℃，20MHz）

（a）氢不去偶的^{13}C-NMR 谱；（b）NOE 增益偶合^{13}C-NMR 谱（门控去偶）

根据^{1}H-NMR 谱中氢信号的积分面积，可进行混合物的定量分析。图 2-11(a)为 2,4-戊二烯酮的^{1}H-NMR 谱，其中含 87%烯醇式和 13%的二酮式。但是全去偶的^{13}C-NMR 谱中，碳信号强度受 NOE 增益和弛豫时间的影响，所以多数情况不能由信号强度进行定量分析。例如，图 2-11（b）中由全去偶^{13}C-NMR 测定上述混合物中烯醇的含量为 81% ~ 93%，偏差较大。利用反门控去偶可解决上述问题，即仅在 FID 信号时进行氢宽带去偶，从而抑制 NOE 影响，信号强度与碳数目有可比性，因此可以用来定量分析如图 2-11（c）所示。

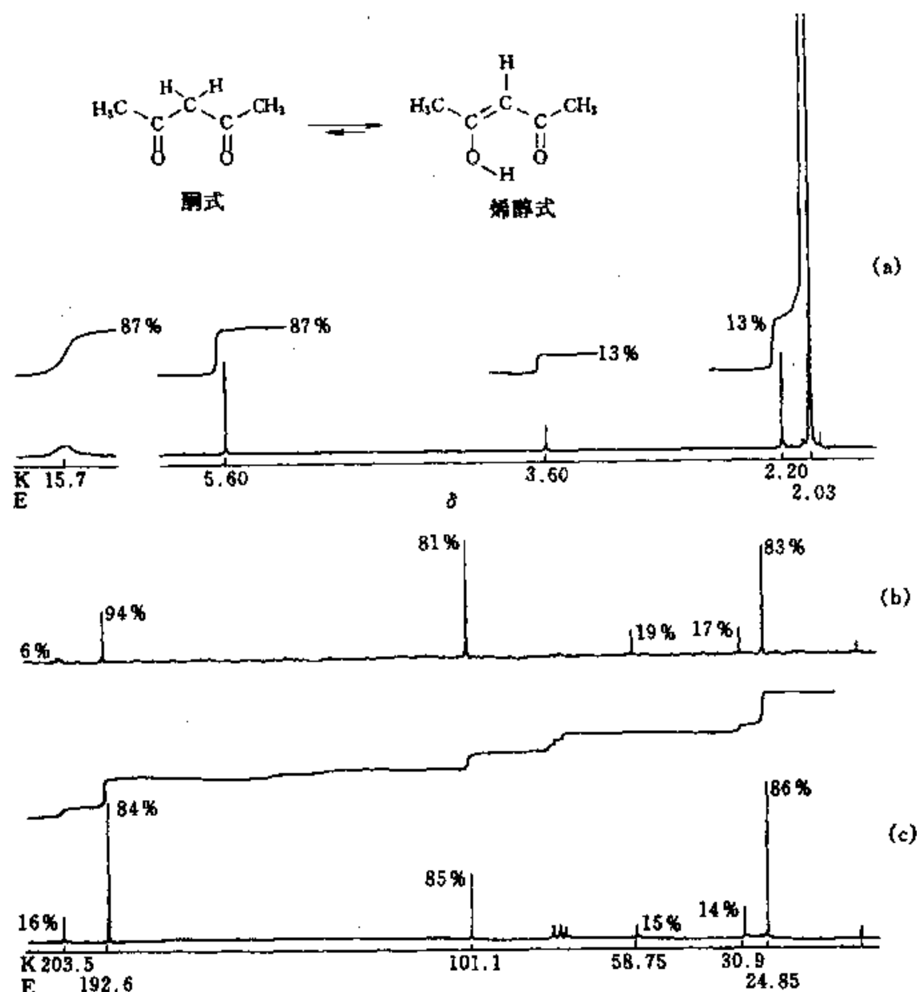


图 2-11　2,4-戊二烯酮的酮-烯醇互变异构体的 NMR 分析

($\varphi CDCl_3$) = 50%, 25℃, ^{1}H-NMR, 60MHz, ^{13}C-NMR 20MHz

(a) ^{1}H-NMR 谱，由积分求出酮:烯醇 = 13:87);

(b) 氢宽带去偶的^{13}C-NMR 谱; (c) 反门控氢去偶^{13}C-NMR 谱，由积分求出酮:烯醇 = 15:(85 ± 1)

六、核欧沃豪斯效应

在去偶实验中引起信号强度的改变（增加或减少）称核欧沃豪斯效应（NOE，又是核 Overhauser 增益的缩写）。在溶液高分辨 NMR 谱中，NOE 的大小决定于偶合核的磁旋比（γ）。在同核氢氢偶合中 NOE 可达 0.5。而在最常见的异核偶合中，如氢宽带去偶的^{13}C-NMR 谱，NOE 可达 1.988，即信号强度可增至 3 倍。在氢宽带和门控去偶的^{13}C-NMR 谱中信号通常增至 2 倍，如图 2-6 和图 2-10 所示。

第三节　核磁共振术语

一、一般术语

核磁矩　nuclear magnetic moment，当核的自旋量子数不等于零时，原子核具有的磁矩。

磁性核 magnetic nuclear，自旋量子数不等于零的核。

磁旋比 （γ）gyromagnetic ratio，核磁矩与其自旋角动量之比。

磁化矢量（M） Magnetization vector，磁场中所有核磁矩矢量的集中体现。

进动 precession，原子核磁矩在静磁场中受到扭矩的作用，由于原子核有自旋运动，这扭距就迫使磁矩围绕磁场方向转动，描绘了一个圆锥形轨迹。

拉摩频率 Larmor frequency，处于静磁场中的原子核磁矩，绕该磁场进动的频率。

自由感应衰减（FID） free induction decay，自旋系统在脉冲作用下，接受线圈中出现感应信号，其强度随时间而衰减。

饱和 saturation，由于高低能极间粒子的快速跃进达到动态平衡，而使共振信号消失的现象。

内锁 internal lock，提供锁信号的核（一般用氘）溶在试样中，与被测试核处在磁极间同一位置上。

外锁 external lock，提供锁信号的核（一般用氘）放在试样之外，与被测试核在磁极间处在不同的位置上。

一级图谱 first order spectrum，自旋系统中，核间化学位移差与它们的偶合常数之比大于或等于 7 时所产生的图谱。

二级图谱 second order spectrum，自旋系统中，核间化学位移差与它们的偶合常数之比小于 7 时所产生的图谱。

旋转边峰 spinning side band，试样管旋转时，由于它所处的磁场不均匀性而引起主峰两侧出现对称的边峰。

化学位移 chemical shift，处于同一磁场中的质子或其他磁性核，由于其在分子中所处的化学环境不同，而在不同的频率下发生共振的现象。或者说，由于分子中的化学不等价性而引起的拉摩频率位移。

偶合常数 coupling constant，描述偶合强弱的参数。在一级图谱中，自旋的谱线间距离等于偶合常数。

参比物 reference compound，放置在试样中，产生的谱线作为化学位移零点的化合物。

内标 internal standard，与试样同时溶于溶剂中，处于磁场的同一位置的参比物。

外标 external standard，与试样分开放置在磁场中的参比物。

屏蔽效应 shielding effect，磁性核在静磁场中，由于它周围电子云的作用，产生一个与静磁场方向相反的磁场，而使该核实际经受的磁场强度小于静磁场强度的现象。

去屏蔽 deshielding，质子核磁共振中，某基团附近由于有一个或几个吸电子基团存在或者该基团处于磁场各向异性基团的特定区域时，使该基团中质子周围的电子云密度降低，屏蔽效应也随之降低的现象。

自旋-自旋偶合 spin-spin coupling，核自旋之间通过成键电子传递的间接相互作用。

自旋-自旋裂分 spin-spin splitting，由自旋偶合引起的谱线分裂现象。

远程偶合 long-range coupling，在质子核磁共振中，核间相隔四个或四个以上键之间的偶合；在^{13}C 核磁共振中，则为相隔两个或两个以上键的核之间的偶合。

弛豫 relaxation，当核自旋系统在某一时刻受到射频场作用，核就处在非平衡态，当频率作用停止后，核自旋系统从非平衡态恢复到平衡态的过程。

横向弛豫 transverse relaxation，核磁化强度在与静磁场垂直方向的分量从非平衡态逐渐

恢复到零的弛豫过程。在该过程中，自旋体系内部有能量交换，而自旋体系总能量不变。

纵向弛豫 longitudinal relaxation，核磁化强度在与静磁场平行方向的分量从非平衡态恢复到平衡态的弛豫过程。在该过程中，自旋体系要和晶格或环境交换能量，自旋体系总能量降低。

弛豫时间 relaxation time，描述核自旋系统从非平衡态恢复到平衡态的弛豫过程所需要的时间。弛豫时间分为纵向弛豫时间（T_1）和横向弛豫时间（T_2）。

氘交换 deuterium exchange，试样中与氧、氮、硫等相连的活泼氢所出现的信号，加进重水后，该信号减弱或消失的现象。

核欧沃豪斯效应（NOE） nuclear Overhauser effect，由于磁性核之间的弛豫作用，当一个核的信号被饱和时，另一个与其有交叉弛豫作用的磁性核的信号强度增强或减弱的现象。

有效相关时间（τc） effective correlation time，分子在连续旋转中为保持其空间取向，相记忆和分子碰撞等所需平均时间的参数。

相干 coherence，相干是磁化量概念的概括，即具有固定相位的核发生旋进并可通过二个能级间的跃迁而交换其自旋态的现象。根据跃迁的 ΔMz，相干可分为零量子数，单量子数，双量子数相干等。单量子数相干可直接被检测出来。

反转实验 Inverse experiments，在异核化学位移相关谱中通过测量高敏核（如^{1}H）的信号而确定低敏核（如^{13}C）信号的方法。

二、方　法

核磁共振波谱法（NMR） nuclear magnetic resonance spectroscopy，研究某些有磁矩的原子核，在静磁场中由于磁矩和磁场相互作用形成一组分裂的能级，在合适频率的射频作用下，能级间发生跃迁而出现的共振现象。

^{13}C核磁共振 ^{13}C nuclear magnetic resonance，研究碳-13 核的核磁共振现象。

质子磁共振 proton magnetic resonance，研究质子的核磁共振现象。

二维谱 two-dimensional spectrum，由两个彼此独立时间域函数经两次傅里叶变换得到两个频率域函数的核磁共振谱。

化学位移相关谱（COSY） correlation spectroscopy，是重要的二维核磁共振谱，通常分同核相关即氢-氢相关谱和异核相关即氢-碳相关谱，以解决分子中氢核与氢核之间或氢核与碳核间的关连。

无畸变极化转移增益法（DEPT） distortionless enhancement by polarization transfer，一种一维极化转移脉冲序列，用以确定分子中碳连结氢的数目，如 CH_3，CH_2，CH，C。

非敏核极化转移增益法（INEPT） insensitive nuclei enhanced by polarization transfer，一种低敏核极化转移脉冲序列，用来确定分子中碳连氢数目。

异核多量子相干谱（HMQC） heteronuclear multiple quantum coherence，一种高灵敏度的反向-键异核相关技术，以测定分子中氢碳直接相连关系。

异核多键相干谱（HMBC） heteronuclear multiple bond coherence，一种高灵敏度反向多键异核相关技术，以测定分子中远程（通常指三键内）氢碳连接关系。

异核远程相干谱（COLOC） correlation via long range coupling，测定分子中远程氢碳关连的方法。

二维核欧沃豪斯效应谱（NOESY） two-dimensional nuclear Overhauser effect correlation spec-

troscopy，研究测定分子中核欧沃豪斯效应的二维谱方法。

低丰度核双量子跃迁实验（INADEQUATE） incredible natural abundance double quantum transfer experiment，一种测定分子骨架中碳原子间连接的技术。

差谱 difference spectroscopy，将双照前后所得的自由感应衰减信号（FID）进行扣除便得到差谱。其中核欧沃豪斯效应差谱（NOED，nuclear Overhauser effect difference spectroscopy）系一种最常见的差谱。

全相关谱（TOCSY） total correlation spectroscopy，一种测定分子中所有偶合氢关系的二维化学位移相关谱。

同核全相关谱（HOHAHA） homonuclear Hartmann Hahn spectroscopy，测定分子中所有相互偶合氢关联的化学位移相关谱。

接力相关谱（RELAY） Relayed correlation spectroscopy，利用多步相干转移而关连分子中偶合氢的技术。

旋转坐标系欧沃豪斯增益谱（ROESY） rotating frame Overhauser enhancement spectroscopy，一种相敏的测定分子中核欧沃豪斯效应的二维谱方法。

碳连氢测定法（APT） attached proton test，利用J-调节自旋回波法测定分子中碳连氢的技术。

三、仪　器

核磁共振波谱仪（NMR） spectrometer，利用核磁共振现象研究化合物结构用的装置。它主要包括磁体、磁场稳定单元、探头、射频发射和接收、波谱显示和记录等部件。

连续波核磁共振波谱仪（CW-NMR） continuous wave NMR spectrometer，射频场连续不断地激发核自旋系统，该系统中只有拉摩频率等于射频频率的核才发生共振，从而直接得到频率域谱的核磁共振波谱仪。

超导核磁共振波谱仪（NMR） spectrometer with superconducting magnet，采用铌钛合金或其他超导材料组成的核磁共振波谱仪。

脉冲傅里叶变换核磁共振波谱仪（FT-NMR） pulsed Fourier transform NMR spectrometer，一个强而短的射频脉冲加到试样上，所产生的频谱能同时激发一定频率域范围内所有核的共振，从而得到时间域的响应函数（自由感应衰减），经傅里叶变换后，则得到通常的频率域谱的核磁共振波谱仪。

探头 probe，位于磁极间隙中，由发射和接收线圈、调谐、匹配及滤波电路组成的信号检测系统的部件。

四、其　他

δ值 δ value，化学位移的标度，并规定零点左侧为正，右侧为负。单位为1。

$$\delta = \frac{\nu_S - \nu_R}{\nu_R} \times 10^6$$

谱宽 spectral width，根据仪器、试样和测量要求所选择的谱带的总宽度。

脉冲序列 pulse sequence，在脉冲傅里叶变换核磁共振实验中，由脉冲程序器根据实验要求而设计的一系列各种不同宽度、不同间隔、不同相位的射频脉冲的组合。

脉冲宽度 pulse width，一个射频脉冲持续作用的时间。

脉冲间隔　pulse interval，两个射频脉冲相隔的时间。

取数时间　acquisition time，一个 FID 信号所需要的时间。数值上等于采样时间与所采的数据点数的乘积。

采样时间　dwell time，采集两个相邻数据点所间隔的时间。

位移试剂　shift reagent，能与试样中的某些基团络合而使邻近基团化学位移产生较大移动的试剂。

弛豫试剂　relaxation reagent，能与试样中的某些基团络合而使邻近基团的弛豫加速但不产生位移的试剂。

氘代溶剂　deuterated solvent，用氘取代各种有机溶剂中的氢的溶剂。

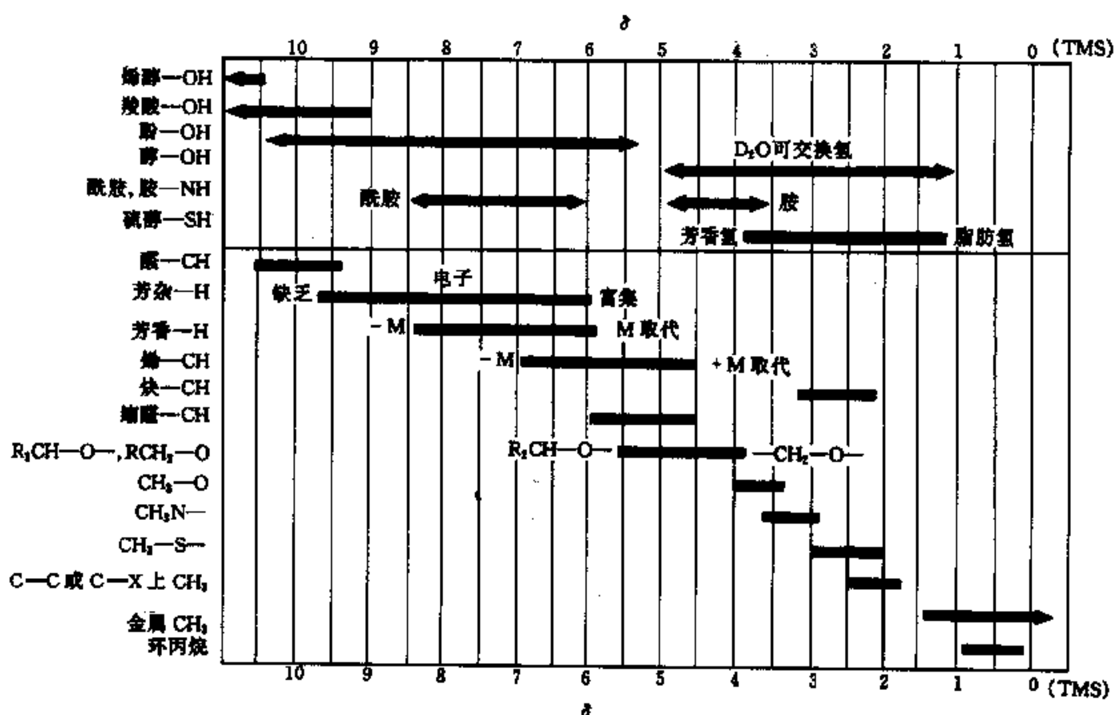
第三章　用一维和二维核磁共振技术确定化合物结构

第一节　官能团的确认[1,2,4]

一、^{1}H 化学位移

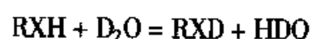
根据^{1}H 的化学位移可以确定分子中存在何种官能团，每种含^{1}H 的官能团都有其较固定的化学位移范围（见表 3-1）。醛基（$\delta=9.5\sim10.5$）；亚甲二氧基（$\delta=5.9\sim6.2$）；缩醛（$\delta=4.5\sim6$）；含氧烷基（$\delta=4\sim4.5$）；甲氧基（$\delta=3.5\sim4$）；*N*-甲基（$\delta=3\sim3.5$）；双键上的甲基，如 C═C 。 C═X （X = N，O，S）或芳环，杂芳环上的甲基（$\delta=1.8\sim2.5$）；乙酰甲基（$\delta\approx2.0$）；环丙烷^{1}H 化学位移处较高场（$\delta\approx0.5$）。根据^{1}H 化学位移可鉴别炔氢（$\delta=2.5\sim3.2$），烯氢（$\delta=4.5\sim6$）以及芳氢或杂芳氢（$\delta=6\sim9.5$）。π-电子富集的吡咯、呋喃、噻吩其化学位移偏小（$\delta=6\sim7$），而 π-电子匮乏的杂芳环（如吡啶）化学位移值偏大（$\delta=7.5\sim9.5$）。

表 3-1　有机化合物^{1}H 化学位移范围



二、重氢交换

连在杂原子上的氢（如 XH，X = O、N、S），其化学位移范围较宽，一般不易识别，但可用重氢交换法确认。



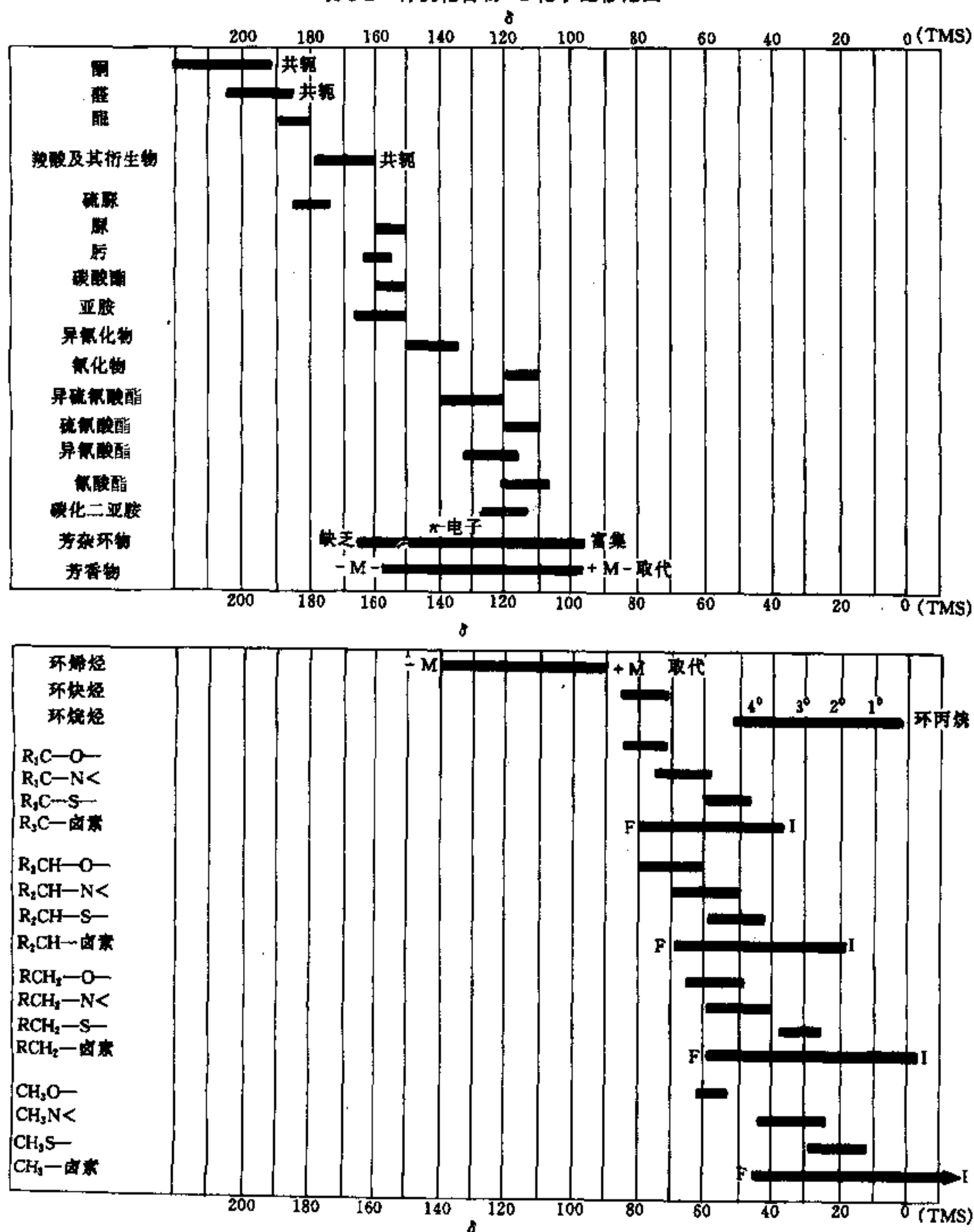
$$RXH + D_2O = RXD + HDO$$

XH 中的氢被交换后在^{1}H-NMR 谱中 XH 信号消失，而出现 HDO 信号，其化学位移 $\delta\approx$ 4.8。有时 CD_3OD 也可用来代替 D_2O 进行交换。

三、^{13}C 化学位移

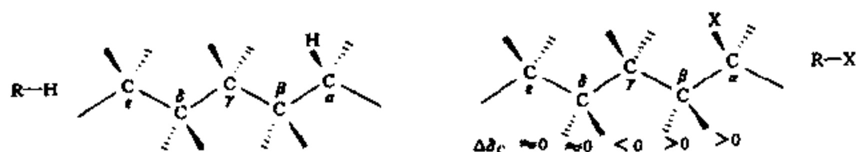
有机化合物含碳官能团各具有特征的化学位移值(见表3-2)，以此可确定这些基团的存在。例如各种类型的羰基呈现不同的化学位移。酮羰基化学位移在190～220之间，环戊酮

表 3-2 有机化合物^{13}C 化学位移范围



的化学位移最大。醛的化学位移在 185~205 之间，有时与酮信号重叠，但可用醛的 C—H 偶合谱双峰加以区别。醌的化学位移在 180~190 范围，而羧基及其衍生物的化学位移通常在 160~180。但苯环连氧碳、碳酸酯、脲、肟及其他亚胺基碳的化学位移也在 160 左右，这些基团的确认必须借助其他方法。其他容易确认的官能团有氰基（δ = 110~120）与异氰基（δ = 135~150）；硫氰基（δ = 110~120）与异硫氰基（δ = 125~140）；氰酸（δ = 105~120）与异氰酸（δ = 120~135）；结合不同杂原子或取代基的脂肪碳（表 3-2），如醚甲氧基的化学位移通常在 55~62 范围，酯甲氧基为 52，*N*-甲基在 30~45，*S*-甲基为 25 左右。化学位移在 20 的甲基信号也可来源于 C═X 或 C═C 上的甲基，如乙酰基 CH_3CO。

烷烃 R—H 上的氢原子被取代基 X 所取代，其 α-位的 δ_C 向低场移动，正比于取代基 X 的电负性，其 β-位 δ_C 一般亦低场移动；然而 γ-位的 δ_C 则高场移动，称 γ-效应。间隔远的碳原子，其化学位移一般不受影响（$\Delta\delta = 0$）。



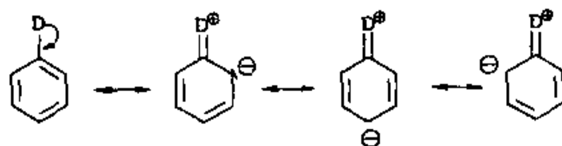
与[1]H 谱不同，一般不用[13]C 化学位移来区别芳环，芳杂环和双键化合物。与[1]H 谱类似之处是 π 电子匮乏的芳杂环（如吡啶类），其[13]C 化学位移比 π-电子富集的芳杂环物（吡咯等）的[13]C 化学位移值大。

烯、芳环和芳杂环上取代基效应对其碳原子[13]C 化学位移的影响，一般可根据其中介效应而粗略预算。所以，连于双键的给电子取代基 D（D = OCH_3、S—CH_3、N—CH_3）可屏蔽其 β-C 和 β-H（δ 变小），称正性中介效应，而其 α-位是去屏蔽的（δ 增大），称负诱导效应。

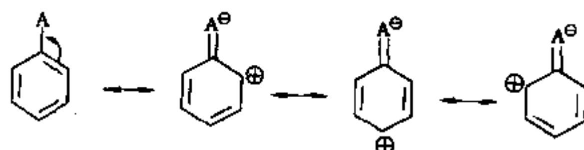


拉电子基团 A（ A═C═O、C≡N、NO_2 ）可使双键反向极化，致使 β 位去屏蔽（负中介），化学位移增大。取代基对芳环和芳杂环的影响类似。给电子基团 D 将使芳环 α-碳原子去屏蔽，对其邻位和对位屏蔽，而间位则基本不影响。

拉电子基团 A 使芳环邻、对位发生反向的极化作用而去屏蔽，化学位移低场移动，间位基本不受影响。



邻位，对位：$\delta_H < 7.26$；$\delta_C < 128.5$



邻位，对位：$\delta_H > 7.26$；$\delta_C > 128.5$

四、^{15}N 化学位移

分子中含 N 的片段和基团的^{15}N 化学位移见表 3-3。表中所用氮的^{15}N 化学位移标度与^{13}C 所用的 TMS 标度极为平行。表 3-3 中所给出的^{15}N 化学位移以亚硝基、硝基、亚氨基、氨基的次序而递减，这是与相应基团的^{13}C 化学位移相一致（表 3-2）。

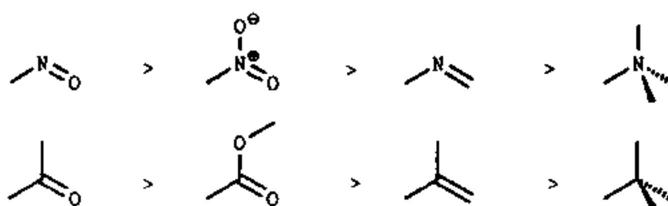
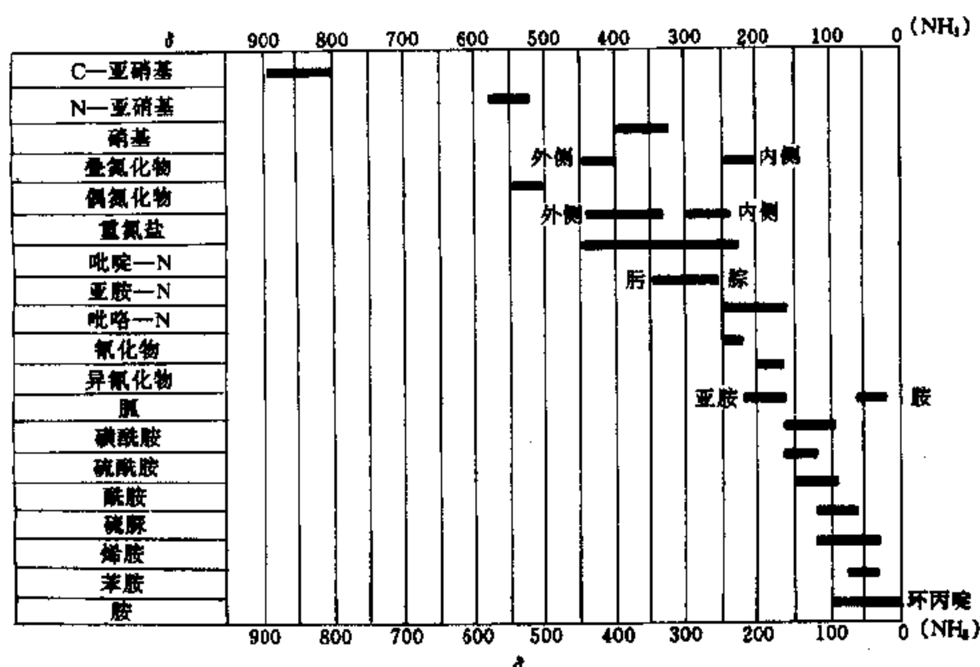


表 3-3 含氮有机化合物的^{15}N 化学位移



其他基团也有类似的性质。

$\delta_{C}:\delta_{烯,芳物}>\delta_{炔}>\delta_{烷}>\delta_{环丙烷}$

$\delta_{N}:\delta_{亚胺,吡啶}>\delta_{CN}>\delta_{胺,氮丙啶}$

第二节 骨架结构（基团间的连接）[3,5,6,9]

一、^{1}H 谱峰多重性

前面已谈过，由于自旋偶合作用，使信号裂分为多重峰。^{1}H 共振信号的裂分常揭示分子中这些氢的相互关系。所以可从多重峰的峰型及峰线数目来鉴定分子中所含的结构单元。一般情况下可应用 $n+1$ 规则（即 $2In+1$ 规则）。

例如，—CH—CH—是最简单的双核单元，AX或AB系统，图3-1给出3个典型例子：(a)为AX系统，其化学位移差值远大于其偶合常数；(b)为AB系统，其化学位移差值与其偶合常数近似；(c)亦为AB系统不过其化学位移差值与偶合常数更靠近。外边两条线将由强的“屋顶”效应而消失。图3-2给出关于结构单元的^{1}H-NMR谱。

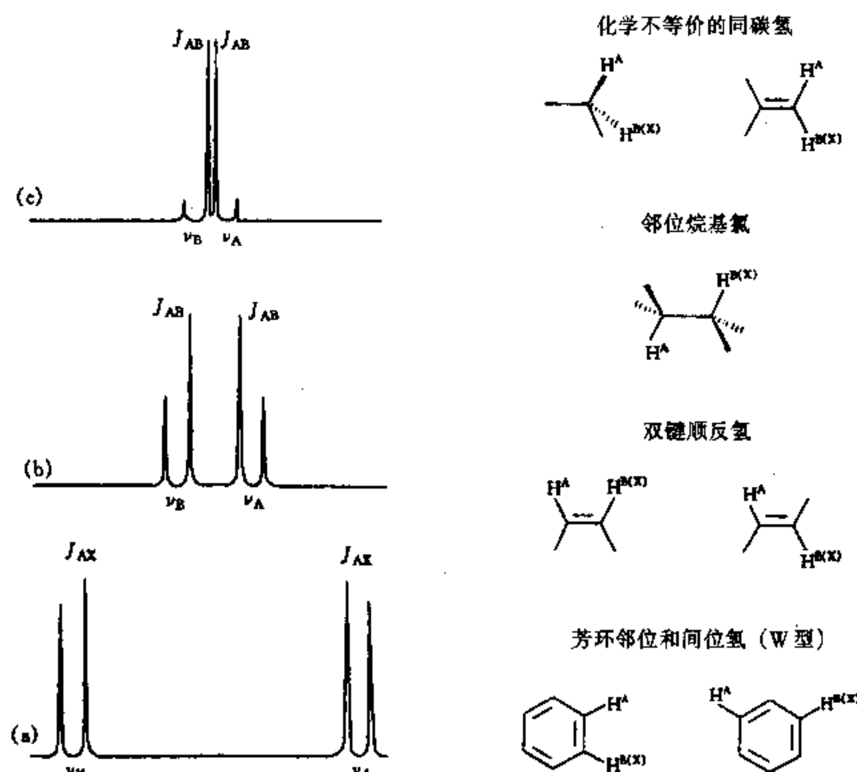


图3-1 AX（AB）系统和典型的分子片段

在结构分析过程中，并不必要弄清复杂谱图中的所有多重峰。如果偶合常数已知，可从简单多重峰的精细结构而确认分子片段，例如，由峰型和偶合常数很易确定烯，芳环或芳杂环的取代类型。

二、C,H峰多重性

由于C—H—键偶合而使^{13}C信号裂分为多重峰，由C—H峰多重性可确定碳原子的取代类型：季碳（R_4C，单峰），三级碳（R_3CH，双峰），二级碳（R_2CH_2，三重峰）及一级碳（R—CH_3，四重峰）。用门控去偶得到的偶合C—H多重峰，因NOE的影响，其信号强度有所增加。但是C—H偶合谱谱线密集，并有重叠，辨认困难，过去曾采用氢核偏共振去偶法解决。在近代核磁共振技术中，多用J-调节自旋回波技术（碳连氢实验，APT）和J-分解二维^{13}C核磁共振谱，并常用一维INEPT和DEPT谱。图3-3为α-蒎烯（1）的J-分解^{13}C-NMR谱。由图清晰看出^{13}C化学位移和J_{C-H}的关系，二者分别在两个坐标轴上，从而避免信号的重叠。

J-调节自旋回波，INEPT和DEPT技术系采用不同的脉冲序列，使^{13}C核发生极化转移，

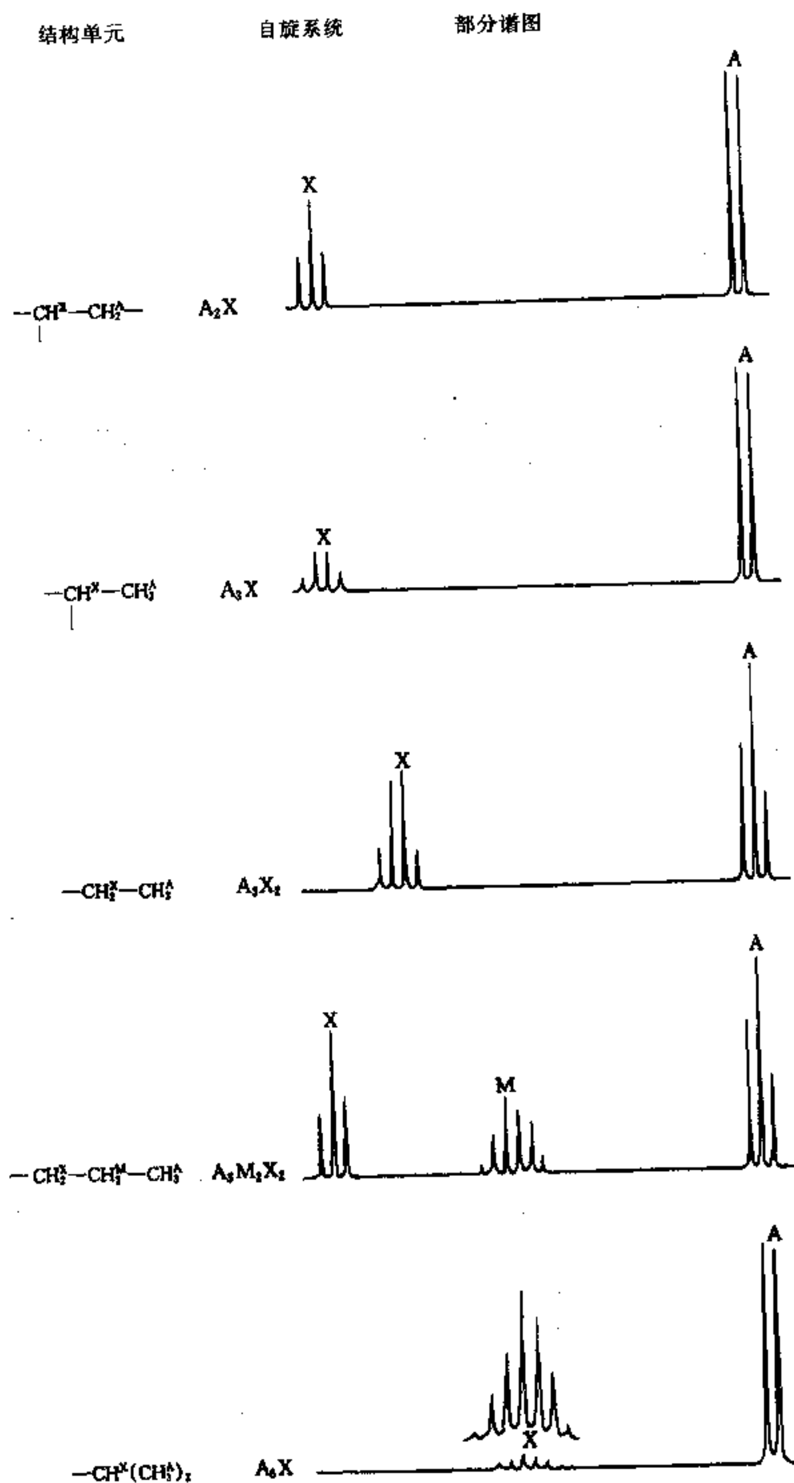


图 3-2　易确认的 A_mX_n 系统及其典型的分子片段

导致 C—H 信号多重性和自旋-自旋偶合的信息发生转移，形成不同相位的氢宽带去偶 ^{13}C-NMR 谱（正，负信号）。INEPT 和 DEPT 技术有利于 ^{1}H-^{13}C 极化转移，从而增加 ^{13}C 强度 4 倍。因此这是测定 ^{13}C-^{1}H 信号多重性的最简便方法。图 3-4 说明利用 DEPT 技术确定 α-蒎烯的 C—H 信号多重性，常规做法是测几种亚谱：图 3-4（a）是 ^{1}H 宽带去偶 ^{13}C-NMR 谱，（b）是 C—H 的 DEPT 谱；（c）是 CH、CH_2、CH_3 的 DEPT 谱，其中 CH，CH_3 为正信号，CH_2 为负信

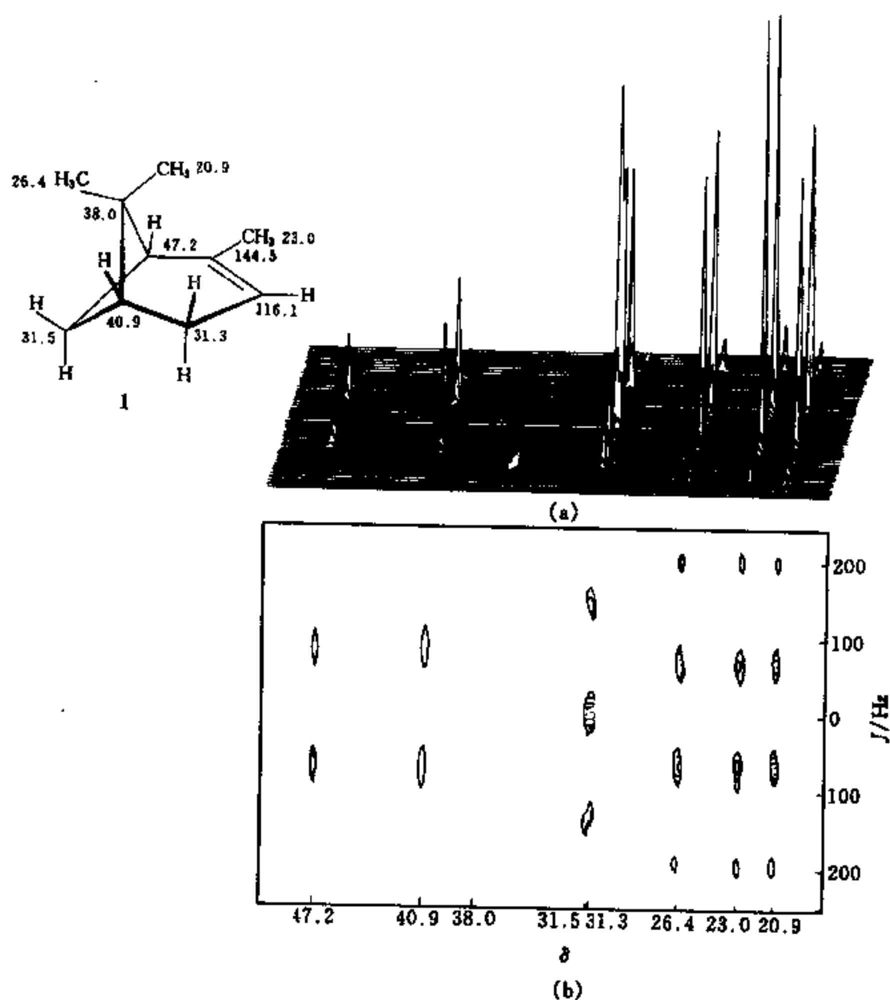


图 3-3 α-蒎烯（1）的 J-分解二维^{13}C-NMR 谱[$(CD_3)_2CO$,25℃，50MHz]
(a) 堆形图；(b) 等高线图

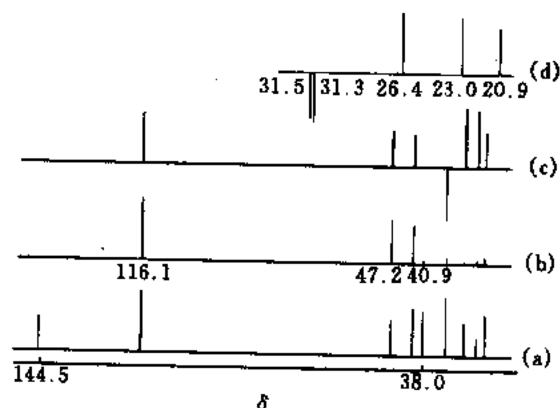


图 3-4 α-蒎烯（1）的 DEPT 谱
(a) 氢宽带去偶的^{13}C-NMR 谱；(b) C—H 的 DEPT 谱；(c) 所有碳原子的 DEPT 谱
（CH 和 CH_3 正信号，CH_2 负信号）；(d) c 谱的部分放大图

号。(d) 部分 (c) 谱的放大谱。季碳信号不出现在 DEPT 谱的亚谱中，因此可从^{1}H 宽带去偶^{13}C-NMR 谱中鉴别。INEPT 技术的脉冲序列不同，所得的谱图形状和分析方法与 DEPT 谱近似也是常用的。

由图 3-4 看出分子中 2 个季碳，3 个 CH，2 个 CH_2 和 3 个 CH_3 信号。

图 3-5 为异松蒎醇 (2) 的^{13}C-NMR 谱，其中 1 个季 C，4 个 CH，2 个 CH_2，3 个 CH_3，加起来为 $C_{10}H_{17}$，经过 CH 平衡后与分子式 ($C_{10}H_{18}O$) 比较少一个 H，因此该物含一个 OH 基。

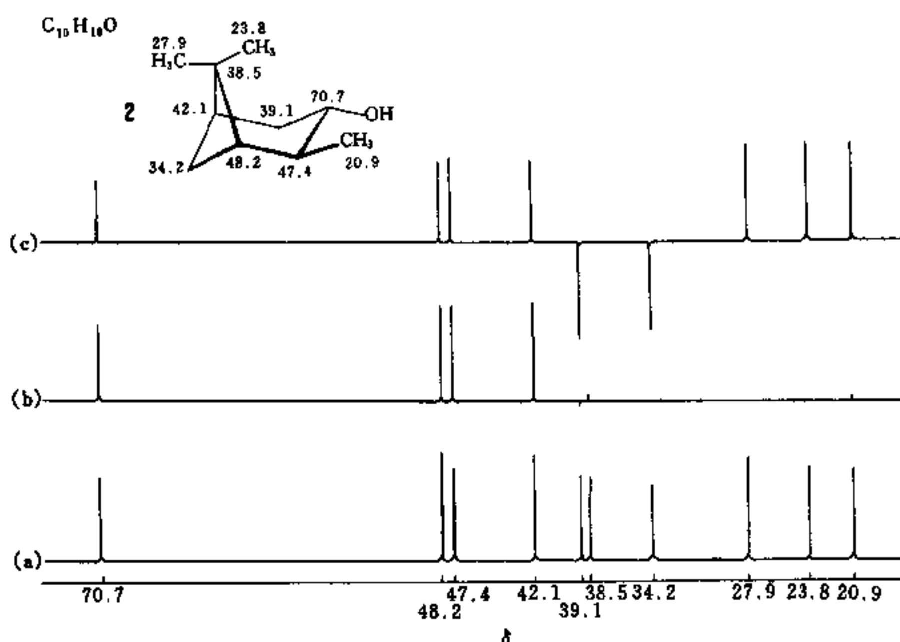


图 3-5 异松蒎醇 (2) 的 DEPT 谱

(a) 氢宽带去偶^{13}C-NMR 谱；(b) CH DEPT 亚谱；

(c) 所有碳的 DEPT 谱 (CH 和 CH_3 正信号；CH_2 负信号；季碳消失)

三、H,H 偶合常数

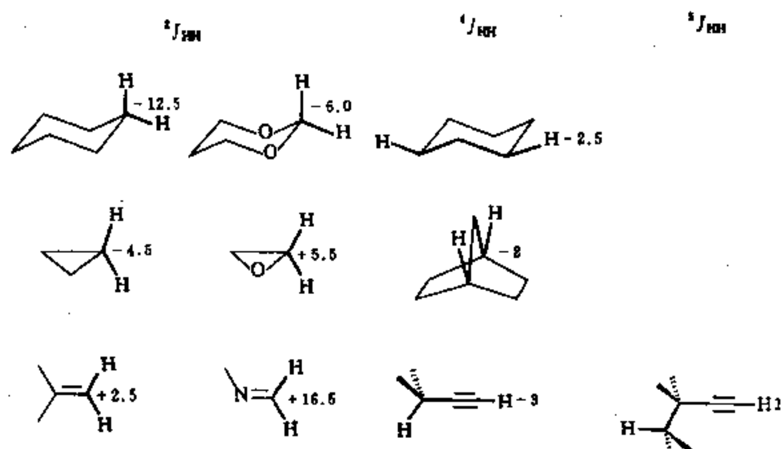
由于自旋核磁矩和成键电子间的互相作用系通过化学键的自旋-自旋偶合而完成的，故偶合常数反映偶合核的成键环境，包括键的种类、性质和相隔键的数目。下面通过二键的同碳氢偶合 (^2J) 和通过三键的邻位氢偶合 (^3J) 进一步加以说明。

同碳氢偶合，$^2J_{HH}$，其大小决定于碳原子的极化和杂化程度，以及取代基种类和 HCH 的键角。用$^2J_{HH}$可鉴别环己烷 (-12.5Hz)，环丙烷 (-4.5Hz)，或末端烯 (2.5Hz) 以及鉴别甲基连有何种电负性杂原子。典型的 HH 偶合见表 3-4。在环己烷和降冰片烷衍生物分子中存在相隔四键的 W 型远程偶合$^4J_{HH}$。邻位偶合常数$^3J_{HH}$对确定相对构型尤为有用。另外$^3J_{HH}$偶合又具有某些其他特征，如电负性杂原子 α-H 具有明显小的$^3J_{HH}$，借此可区别呋喃、噻吩、吡咯和吡啶等芳杂环化合物。

苯环和萘环的邻位 ($^3J_{HH}=7$Hz)、间位 ($^4J_{HH}=1.5$Hz) 和对位 ($^5J_{HH}\leqslant 1$Hz) 氢偶合常数对确定取代基位量极为有用。在萘及其他芳多环 (或芳杂环) 系列中，折型偶合 ($^5J_{HH}=0.8$Hz) 有助于取代类型的确认。

吡啶环的HH偶合与氢的位置密切相关，2-H 和 3-H的偶合($^3J_{HH}=5.5$Hz)明显区别

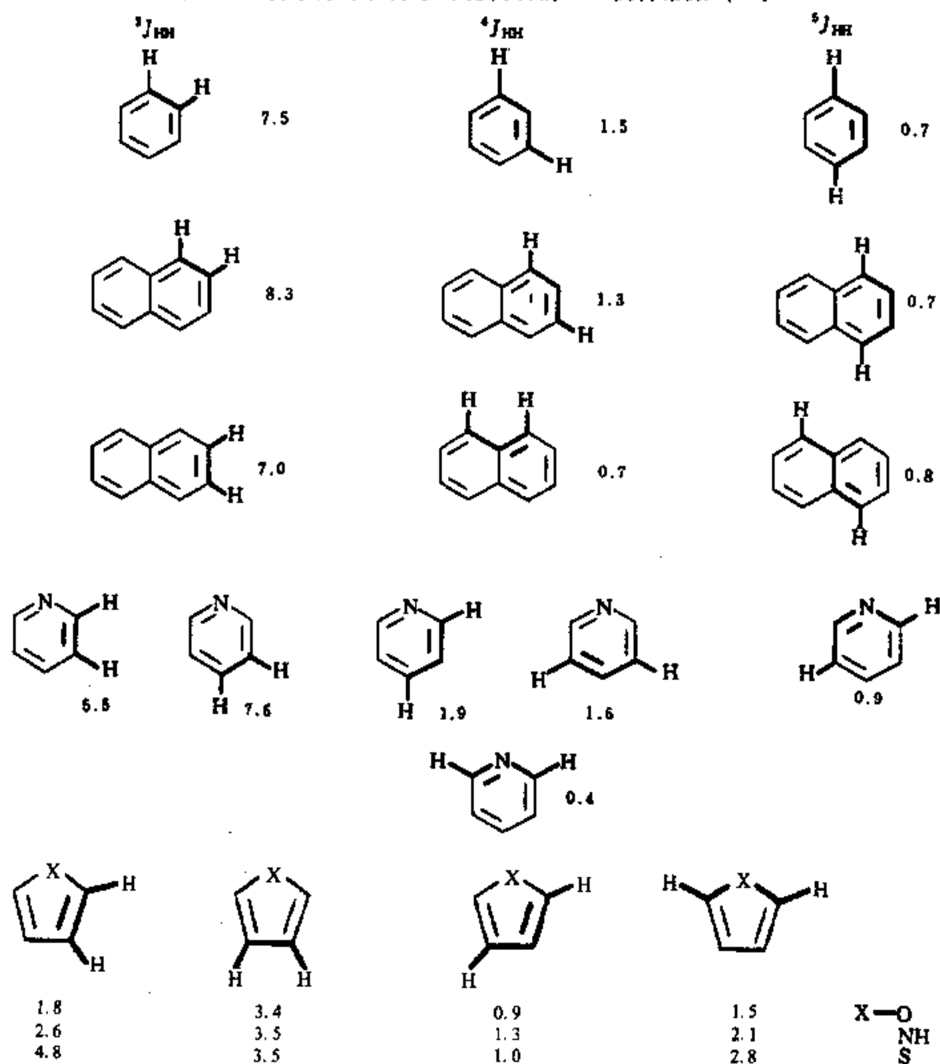
表 3-4 若干典型脂环、烯和炔基团的 HH 偶合常数（Hz）



于 3-H 和 4-H 的偶合$^3J_{HH}=7.6$Hz）。五元杂芳环化合物亦有类似的偶合性质，2-H 和 3-H 的偶合明显小于 3-H 和 4-H 的邻位偶合。

表 3-5 为一些芳环和芳杂环化合物的 HH 偶合常数。

表 3-5 若干芳环和芳杂环化合物的 HH 偶合常数（Hz）



在芳环、芳杂环以及烯烃化合物中，由单一多重峰的分析，往往可清晰确认其取代类型。例如，在苯环氢的化学位移范围（6.5～8.5）有4个氢（由积分强度确定），表明是二取代苯。仔细分析多重峰的峰型及偶合常数，可确定二取代基的位置。

图3-6给出三种典型的二取代苯^{1}H-NMR多重峰。在图3-6（a）中$\delta=6.8$和7.5的三重双峰是很特征的，表明2个邻位偶合（8.0Hz和7.0Hz）和1个间位偶合（2.5Hz），即每个H有2个邻位质子，所以必须是邻位二取代苯（邻硝基苯酚，3）。

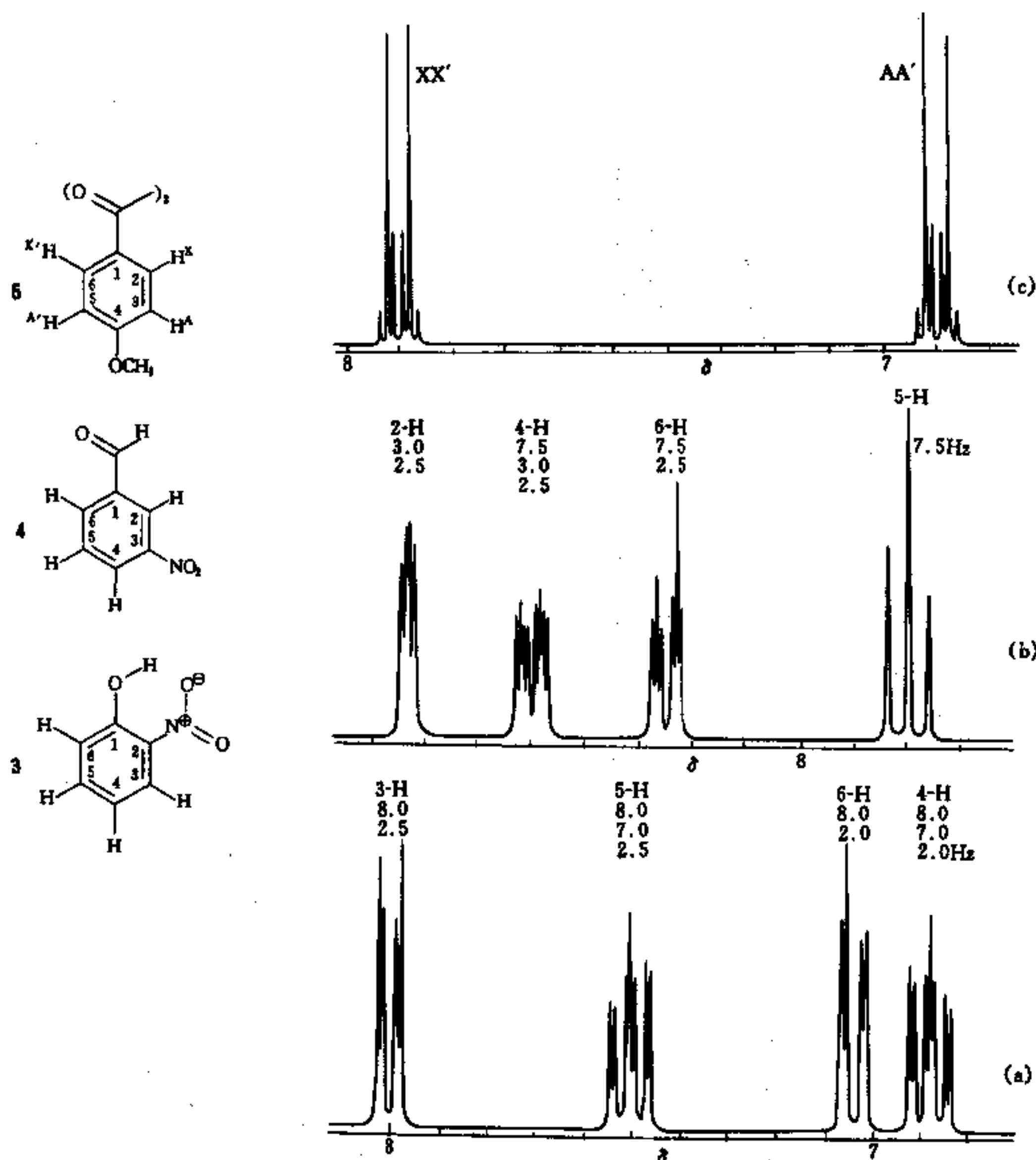


图3-6 二取代苯的^{1}H-NMR谱（$CDCl_3$，25℃，200MHz）
(a) 邻硝基苯酚（3）；(b) 间硝基苯甲醛（4）；(c) 4,4'-二甲氧基联苯酰（5）

在图3-6（b）中$\delta=7.8$的峰仅显示2个邻位偶合（$^3J_{HH}=7.5$Hz），而$\delta=8.74$信号仅显示2个间位偶合（$^4J_{HH}=3.0$Hz和2.5Hz），前者（$\delta=7.8$）是1个三重峰，来自2个相等的^3J；而后者（8.74）是2个双峰，因为有2个不等的^4J。

图3-6（c）所示的AA'XX'系统，从其对称的多重峰型很容易辨认，是对位二取代苯的

特征，如4,4′-二甲氧基-联苯酰（5）或4-取代吡啶。

通过仔细分析多重峰的精细结构来确定芳环或芳杂环等的取代类型是简便易行的。在具体分析的过程中，要注意运用偶合核具有相同偶合常数的原理，即相互偶合是对等的。因此，一旦某个多重峰的偶合常数被确认，则可从另外多重峰的峰型及偶合常数确定其偶合类型。图3-7和图3-8是具体实例。图3-7给出两种不同磁场强度的三取代苯衍生物的^{1}H-NMR谱，在典型芳环化学位移范围的信号$\delta=7.1$呈现2个双重峰，J值为8.5Hz（$^3J_{HH}$，邻位偶合）和2.5Hz（$^4J_{HH}$，间位偶合）。说明该H有两个邻居，一个为邻位，另一个为间位，符号1,2,4-三取代苯AMX类型（6）。然而由此并不能排除1,2,3-三取代苯类型（7）。但是，如

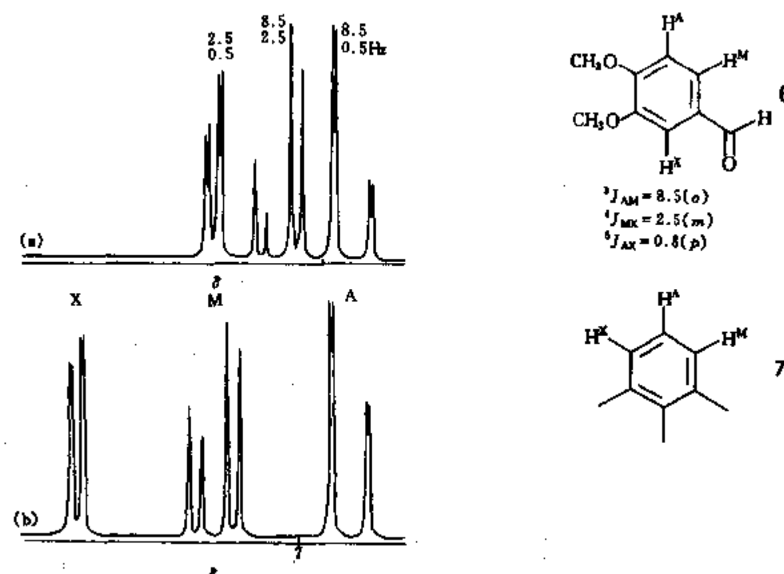


图3-7　3,4-二甲氧基苯甲醛（6）的^{1}H-NMR谱（芳氢部分，$CDCl_3$，25℃）
（a）100MHz；（b）200MHz

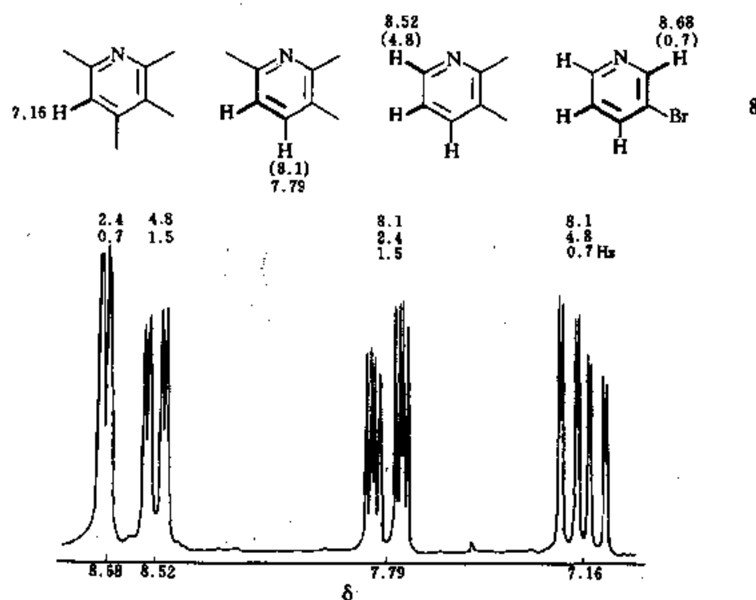


图3-8　3-溴吡啶（8）的^{1}H-NMR谱（$CDCl_3$，25℃，90MHz）
结构式中括号内的数据为偶合常数。

为后者，则 A 核应有两个邻位偶合，这是与图 3-7 不符合的。根据偶合核具有相同偶合常数的原理，可对图中的偶合常数进行归属。邻位偶合$^3J_{AM}$ = 8.5Hz，δ = 6.93 为 H_A；间位偶合，$^4J_{MX}$ = 2.5Hz，δ = 7.28 为 H_x，对位偶合$^5J_{AX}$ = 0.8Hz，由于数值较小通常是难于观察的，高场核磁尤其如此。

图 3-8 为单取代吡啶的^{1}H-NMR 谱，其最小化学位移 δ = 7.16 裂分为 1 个三裂双峰，偶合常数分别为 8.1、4.8 和 0.7Hz，由 2 个$^3J_{HH}$偶合（8.1Hz 和 4.8Hz）可归属该氢为吡啶环的 β-H。逐步归属所有 3 个偶合常数可明确推导出该化合物为 3-取代吡啶衍生物的结论（8），由此并结合偶合相互对等的原理可对其他信号进行归属。

四、C,H 偶合常数

一键的 C—H 偶合常数（$^1J_{CH}$）正比于偶合碳原子杂化轨道中 s 成分的比率（表 3-6），可计算如下：

J_{CH} = 500 × s，其中 s = 0.25（sp^3），0.33（sp^2）和 0.5（sp）

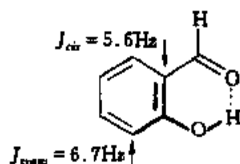
表 3-6　若干结构片段的典型一键 CH 偶合常数 J_{CH}/Hz

碳杂化度	sp^3：H 125	sp^2：H 160		sp：≡—H 250
电负性	N—C—H 140	N=C—H 180	N=C(N)—H 205	N≡—H 269
	O—C—H 145	(O)₂C—H 170	O—C=H 200	
环系大小	H 161	H 134	H 129	H 125
	H 176	H 150	H 145	H 140

由此可区别脂肪碳（J_{CH} = 125Hz）、烯烃碳和芳碳（J_{CH} = 165Hz），炔碳（J_{CH} = 250Hz）。对杂原子取代碳，随杂原子电负性增加，其 J_{CH}递增。典型的 J_{CH}如下：环丙烷的 $J_{CH} \approx$ 160Hz；环氧的 J_{CH} = 170Hz；末端炔的 J_{CH} = 250Hz；烯醇醚的 J_{CH} = （195 ~ 200）Hz（呋喃、吡酮、异黄酮）；2-未取代吡啶和吡咯的 J_{CH} = 180Hz；2-未取代嘧啶 J_{CH} > 200Hz。

二键的 C—H 偶合常数$^2J_{CH}$明显减少，并随 C—C—H 键的夹角和偶合碳杂原子取代基的电负性有关，电负性和夹角增加均使$^3J_{CH}$正值增加。

邻位 C—H 偶合$^3J_{CH}$与偶合碳和氢的构型和取代基的性质及位置有关。偶合碳上电负性取代基引起$^3J_{CH}$增加，而减少未偶合碳的$^3J_{CH}$。在可交换的 X—H（X = O，N，S）和碳原子间通过二或三键的偶合（$^2J_{CH}$或$^3J_{CH}$）只有形成氢键时才可观察到，例如水杨醛（10）可看到$^3J_{CH}$偶合。

10 

典型结构片段的$^{1}J_{CH}$，$^{2}J_{CH}$和$^{3}J_{CH}$见表 3-6，表 3-7，表 3-8 和图 3-9。

表 3-7 典型结构片段的二键 CH 偶合常数，$^{2}J_{CH}$/Hz

键角	109.5° COOH H -6.2	120° CH_3 COOH H H 3.1	H COOH CH_3 H 3.4	
偶合碳上电负性取代基	F H -4.9	Cl H -3.4	Br H -3.4	I H -2.5
	O H 11.0	H N H 8.7	S H 7.6	
CX 双键和炔键	N— H 7~9	O H 25	O H 25~30	H 40~50

表 3-8 典型结构片段的相隔三键 CH 偶合常数，$^{3}J_{CH}$/Hz

相对构型	7.5 H CH_3 12.5 H H	H 7.6	H 6.7	4.7 H
偶合碳上电负性取代基	9.1 H CH_2Br 15.5 H H	OH H 9.7	NH_2 H 8.6	CH_3 H 7.5
偶合键中电负性取代基	4.6 H CH_3 8.9 H Br	OH H 4.7	NH_2 H 5.4	CH_3 H 6.6
孤电子对的影响	N H 6.7	N H 5.7	N 6.4 H	11.7 H N

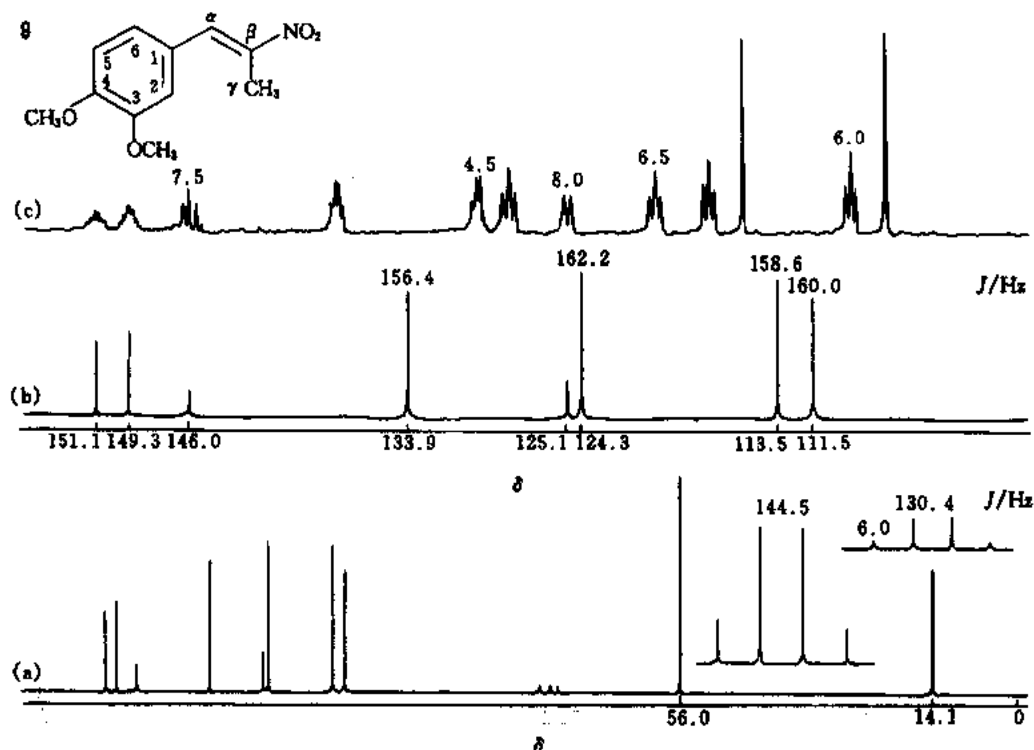


图 3-9　3,4-二甲氧基-β-甲基-β-硝基苯乙烯（9）的^{13}C-NMR 谱（$CDCl_3$，25℃，20MHz）
(a)，(b) 氢宽带去偶；(c) 偶合谱（门控去偶）

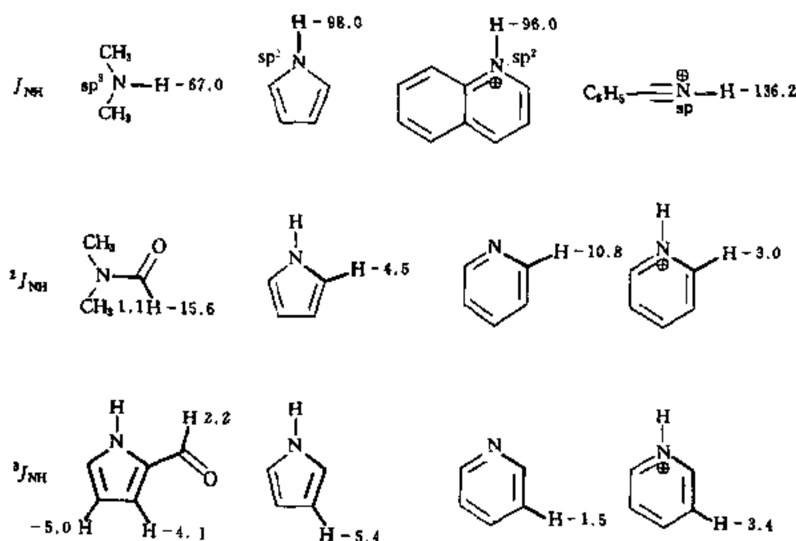
各碳信号归属如下：

C	δ_C/ppm	J_{CH}/Hz	$^{3(2)}J_{CH}$/Hz	偶合氢
C-1	125.1		8.0	(5-H)
C-2	113.5	158.6	6.0	(6-H，α-H)
C-3	149.3			(3-H，5-OCH_3)
C-4	151.1			(2-H，6-H，4-OCH_3)
C-5	111.5	160.0		
C-6	124.3	162.2	6.5	(2-H，α-H)
C-α	133.9	156.4	4.5	(2-H，6-H，β-CH_3)
C-β	146.0		7.5	(α-H，β-CH_3)
C-γ	14.1	130.4	6.0	(α-H)
$(OCH_3)_2$	56.0	144.5		

五、N，H 偶合常数

同^{1}H 和^{13}C 核相比，^{15}N 核磁矩是很小的，并是负值。相应地，NH 偶合常数也是小的，而且其值与 HH、CH 偶合值反向，一键 NH 偶合$^1J_{NH}$正比于连 N 碳杂化轨中的 S 成分比率，由此可区别氨基和亚氨基 NH。甲酰胺具有大的$^2J_{HC}$偶合常数，以此可用来进行鉴别。吡咯和吡啶的$^2J_{NH}$和$^3J_{NH}$明显不同，反映 N 上孤电子对的取向不同（吡咯 N 上的孤电子对垂直于环平面，而吡啶则在环平面中），借此可进行杂环化合物的鉴定。表 3-9 为一些典型结构中的 NH 偶合常数。

表 3-9 典型结构片段的 NH 偶合常数



六、H,H 相关二维核磁共振谱（HH-COSY）

H,H 相关二维核磁共振谱(HH-COSY)技术在结构阐明中起到广泛自旋去偶作用。COSY 谱把分子中偶合氢的化学位移关联起来。在二维实验中两个频率轴均以^{1}H 化学位移标度，结果形成正方形谱图（见图 3-10)。一维^{1}H-NMR 谱的投影呈现在对角线上（对角线信号)。相关信号或偏对角线信号（交叉信号）关联相互偶合的氢核，所以 COSY 谱指明 HH 连接问题，即说明分子中同碳氢、邻位氢和 W 型氢偶合关系及其相关的结构单元。

HH-COSY 谱有两种表示方法,堆形图[图 3-10(a)]和等高线图[图 3-10(b)]。前者属三维空间图，其三维给出信号强度，但由于透视图的变形和重叠，解析起来较难。等高线图解析容易，信号强度由各种不同横切面大小表示[图 3-10(b)]，但是横切高度的选择会影响HH-COSY 谱所提供的信息量，如果横切面太低，则可能切进弱的杂质信号或噪音信号。

从HH-COSY 谱的等高线图中可鉴定分子中各种相互偶合的氢原子,凡是相互偶合的 H 皆可从两个对角线信号和两个偶合对的交叉信号加以确认,偶合对构成正方形的四角。特定核的偶合对信号出现在相应^{1}H 信号的垂直或水平坐标线上。例如,在[图3-10(b)]中，$\delta=8.76$ 质子的偶合对，可从垂直或水平坐标线上找到，该质子是喹啉（11）的 2-H。由于该分子吡啶环的 2-H（$\delta=8.76$）和 3-H（$\delta=7.16$）可从其邻位偶合常数$^{3}J=5.5$Hz 鉴定。从 HH-COSY 谱可证明结构式 11a 中吡啶环的位置。喹啉的 4-H（$\delta=7.90$）呈现另一个交叉信号 $\delta=8.03$，该信号源于苯环的 8-H，由于折线型偶合而与 4-H 关联（11b)。

从 $\delta=8.03$ 信号找到另外两个交叉信号 $\delta=7.55$ 和 7.35，从而确定喹啉中剩下的其他质子（11c)。

从这个例子也可看出 HH-COSY 谱存在一定的局限性。首先如不知化学位移或可能的偶合关系，要做出结论性的判断是很难的，因为交叉信号的面积并不完全显示存在何种类型的偶合。其次，重叠信号，如 $\delta=7.55$ 和 $\delta=7.60$（图 3-10）在 HH-COSY 谱中不能分开，难于判断二者相互偶合。但是如有足够分辨率，多重峰的精细结构，可从对角线和交叉信号的外型加以确认。如图 3-10 中的 $\delta=7.55$ 是 1 个三重峰，而 $\delta=7.60$ 信号则为 1 个双峰。见图 3-10 中 $\delta=$（7.55～7.66）对角线信号的外型。

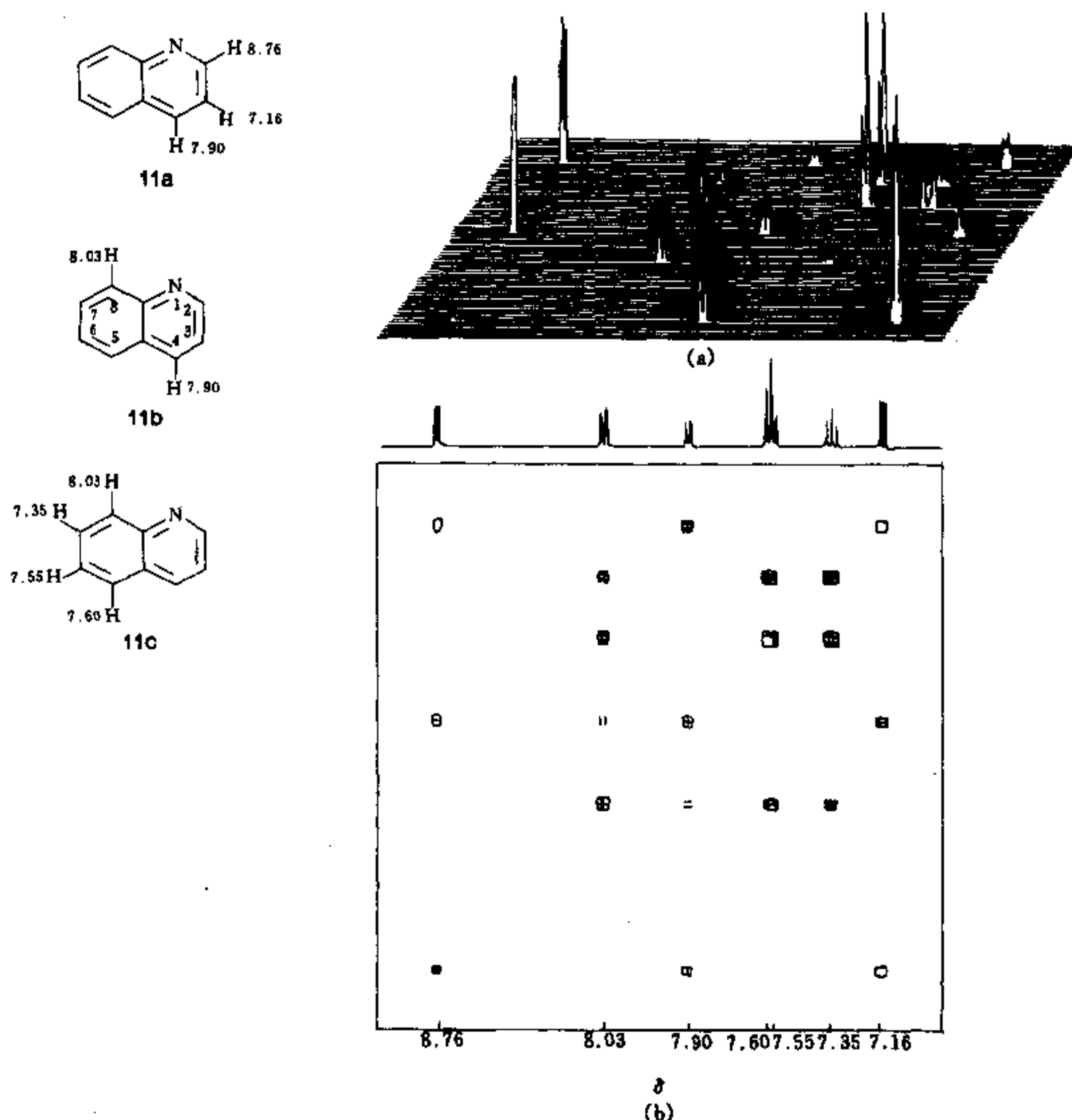


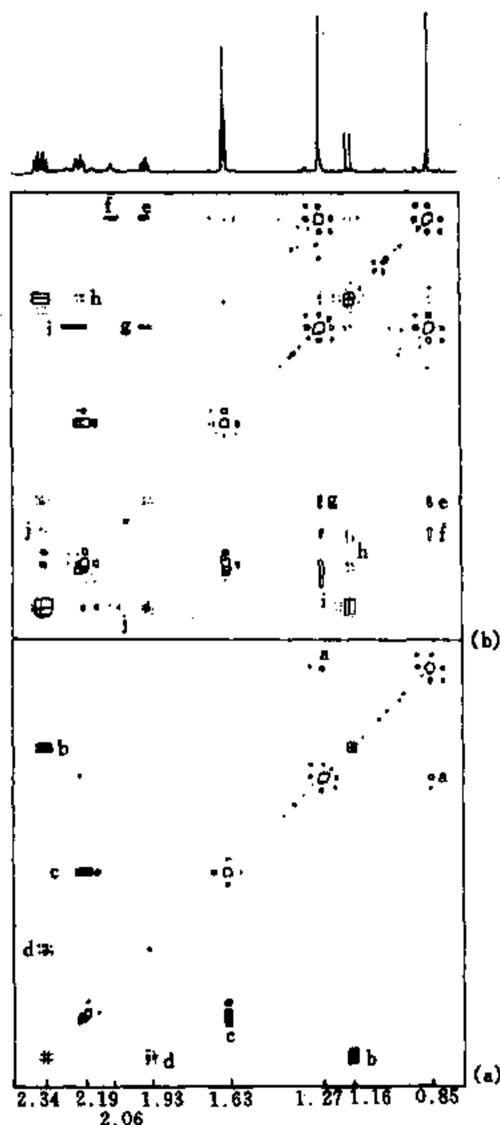
图 3-10 喹啉（11）的 HH-COSY 谱[$(CD_3)_2CO$, $\varphi = 95\%$，25℃，400MHz]

(a) 堆形图；(b) 等高线图

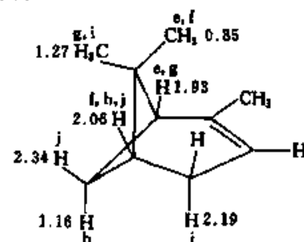
在一维^{1}H-NMR 谱的 n 重裂分情况下，HH-COSY 谱给出 n 重裂分交叉信号，信号的清晰度决定于谱图分辨率。如果多重峰中存在几个小的偶合常数，HH-COSY 谱交叉信号的强度则分布为许多多重峰信号，因此，即便在低层横切，在等高线图中也难于看到交叉信号。

在 α-蒎烯[图 3-11(a)]的 HH-COSY 谱中，看不到 $\delta = 2.06$ 的桥头质子偶合对交叉信号，这是因为前者被许多弱偶合质子小偶合裂分成一个多重峰的关系。在这种情况下，可采用改进的 HH-COSY 实验，如 TOCSY 谱（全相关谱）或者延时 COSY 谱。图3-11(b)为改进的 HH-COSY谱，重点强调小偶合核间的连接作用。例如普通 HH-COSY 谱仅观察 H_a-H_d 的连接，而延时 COSY 谱则观察另外的 H_e-H_j 的连接（图 3-11）。

尽管 HH-COSY 谱存在一些不足，但它总是一种确定结构片段的有效的方法，如再结合其他的二维 NMR 技术，则可推导出完整的结构。



由(b)得：



由(a)得：

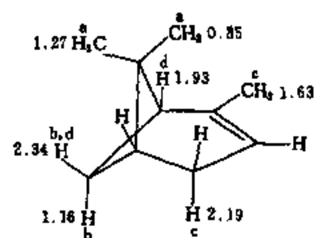


图 3-11 α-蒎烯 (1) HH-COSY 谱的等高线图 [纯度 98%，$(CD_3)_2CO$，$\varphi=10\%$，25℃，400MHz]
(a) 未有延迟时间；(b) 有延迟时间

七、碳碳连接技术（INADEQUATE 方法）

如已知分子中C—C键的连接，则可确定分子的骨架。测定C—C间的偶合常数是确定C—C骨架的有效方法，因为相互偶合碳具有相同的偶合常数，但是测定C—C间的偶合常数是复杂的，受到下列因素的影响。首先^{13}C-^{13}C偶合常数有一些是近似的，尤其是脂肪碳化合物近于相同，出现在35～40Hz范围；再者，^{13}C-^{13}C偶合需要两个核直接相联。但是由于^{13}C核的天然丰度仅为10^{-2}，^{13}C-^{13}C键的可能性仅为10^{-4}，所以在谱图中由于^{13}C-^{13}C偶合的裂分是很弱的，其强度仅为0.5%左右，通常以卫星峰形式隐藏在^{13}C-^{13}C偶合常数中间，靠近^{13}C-^{13}C主要信号（99%强度）的噪音中。改进的一维INADEQUATE实验能抑制^{13}C-^{13}C主要信号，由此在一维谱中所有^{13}C-^{13}C键形成AX和AB系统。根据各核的双量子跃迁频率（$^{13}C_A$和$^{13}C_B$化学位移总和），用二维技术分离这些AB系统而构成二维INADEQUATE谱。用简单正丁醇为例说明该法的应用。图3-12(a)为正丁醇的二维INADEQUATE谱，横坐标为^{13}C

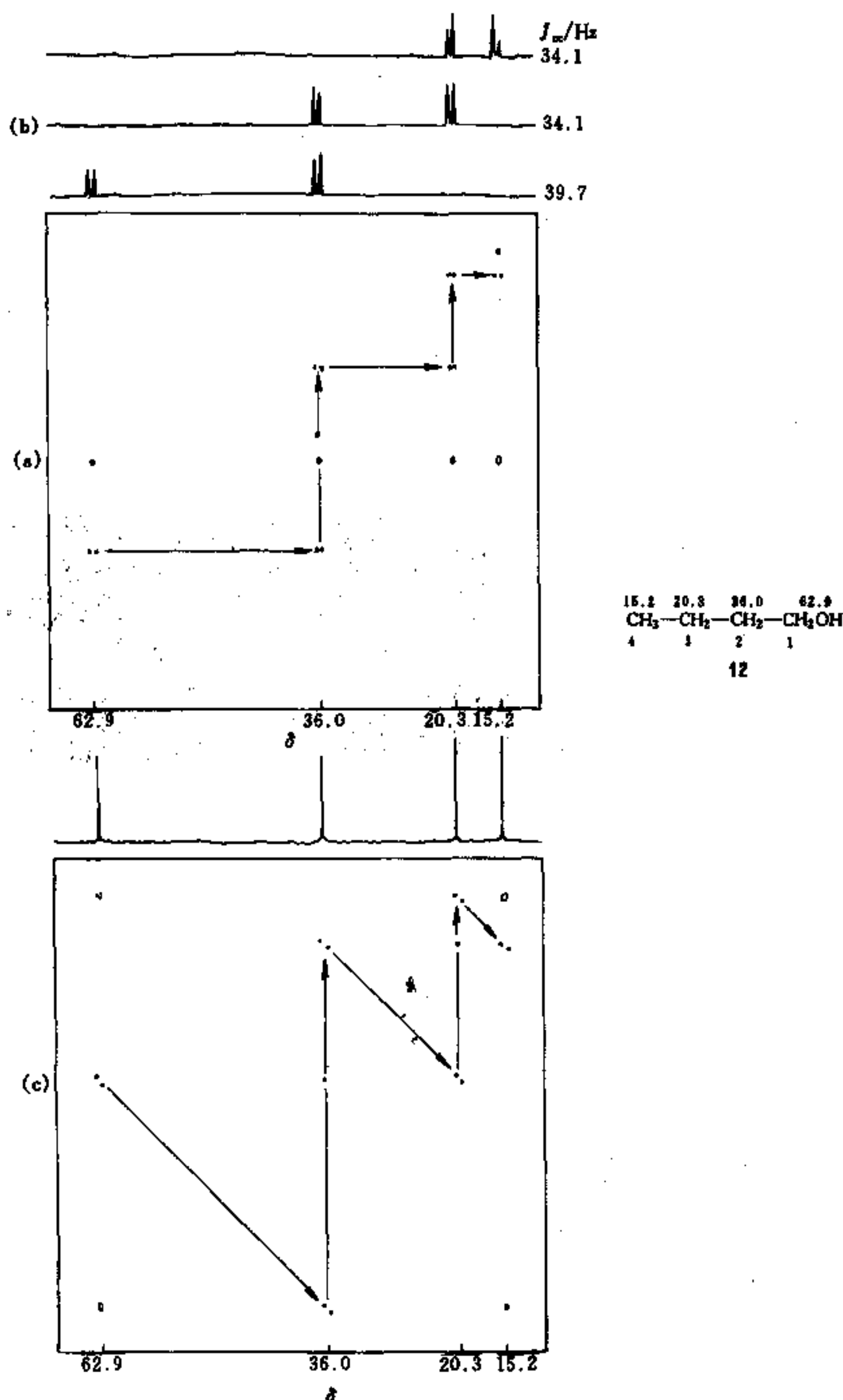


图 3-12 1-丁醇（12）的二维（2D）INADEQUATE 谱[$(CD_3)_2CO$, $\varphi=95\%$，25℃，50MHz]

(a) 在横坐标轴上结合碳原子的 AB 系统等高线图；(b) 分子中 3 个 AB 系统图示；

(c) 对称的 INADEQUATE 谱的等高线图

化学位移，纵坐标为双量子跃迁频率。图中的等高线图为每个 C—C 键的 AB 系统，并与每个 C—C 键的双量子跃迁频率相当。每个 AB 系统可从一维谱图3-12(b)中归属。根据图中的箭头方向便可确定正丁醇分子的碳骨架。

图3-12(c)是另一种 INADEQUATE 谱的表示法，采用类似 HH-COSY 形式，即对角线信号和交叉信号为方型对称。图中示出结合碳原子的 AB 或 AX 系统，交叉信号与对角线信号垂直。一维的 ^{1}H 宽带去偶 ^{13}C-NMR 谱放在对角线信号上方，而分子中所有 C—C 键的 AB 系统与其垂直正交，由此每一个 C—C 键可由其对角线信号和偏对角线的 AB 偶合对构成一个正方形，类似于 HH-COSY 的图型。

INADEQUATE 技术的缺点是灵敏度低，但是如有足够量的样品［每个 C 原子（5～10mg）］，足够大的溶解度，测试时间长些还是可以应用的有效方法。

图 3-13 为异松蒎醇（2）的对称二维 INADEQUATE 谱，由其等高线图可清楚找出分子中碳碳间连接关系。

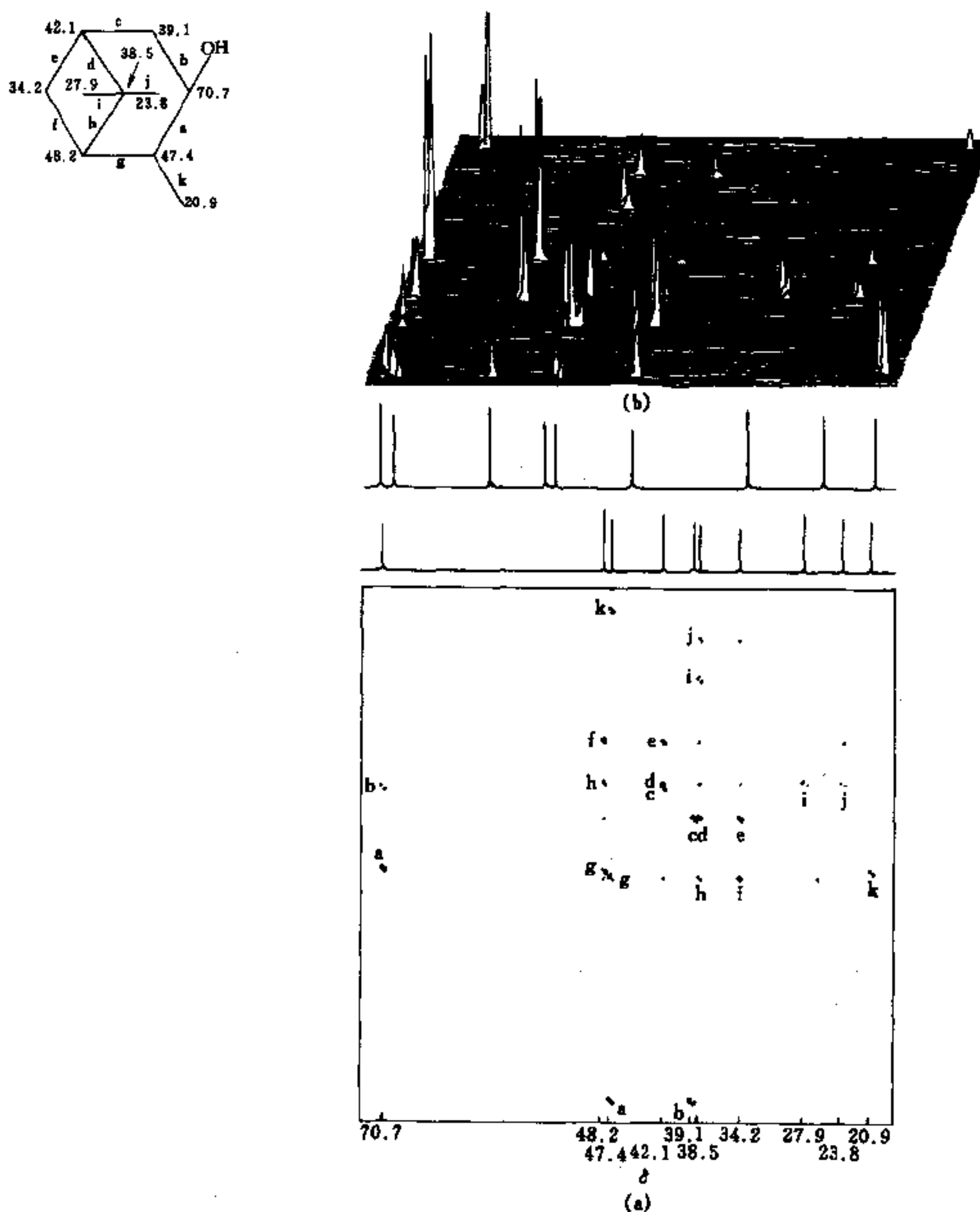


图 3-13 异松蒎醇的对称二维 INADEQUATE 谱［$(CD_3)_2CO$ 250mg 溶在 0.3ml 中，25℃，50MHz］

（a）等高线图，图中 a-k 表示分子中 11 个 C—C 键，很易加以归属；

（b）从 δ＝（20.9～48.2）ppm 间的部分堆形图

八、C,H 相关二维核磁共振谱（CHCOSY）

CH 相关二维核磁共振谱（CHCOSY 谱）有两种检测方法，氢去偶碳检测或碳去偶氢检测，后者灵敏度高，又称反 CHCOSY 或 HMQC（异核多量子相干）法。在 CHCOSY 谱中，两个频率坐标，一个是^{1}H化学位移（通常为纵坐标，或者二者相反），另一个是^{13}C化学位移（通常是横坐标，或二者相反）。CHCOSY 通常指一键 CH 相关，其相关点系通过二维谱中的等高线图确认，见图 3-14。记录 CHCOSY 的脉冲序列包含极化转移。而极化转移是 DEPT 谱的基础，由此可提高灵敏度 4 倍。所以 CHCOSY 实验所需样品量与^{1}H宽带去偶^{13}C-NMR 谱相似。CHCOSY 谱的分析较易，从相关信号找出两个坐标上的^{1}H和^{13}C化学位移即可。例如图 3-14(c)中，$\delta = 1.16$ 的质子（H_A）和 $\delta = 2.34$ 的质子（H_B）为 AB 系统，是与 $\delta = 31.5$ 的 C 原子结合。图 3-14 给出 α-蒎烯（1）分子中所有的 CH 连接。

CHCOSY 技术也是倍受重视的，因为它能明确归属分子中所有 CH 连接问题，而且费时不多。当^{1}H-NMR 谱中存在重叠信号多重峰不易归属时，而其^{13}C-NMR 信号一般总是间隔清晰，便于进行归属，例如甾体或三萜分子中的 CH_2 归属特别有用。如果^{1}H-NMR 谱的分辨率高，则可分析^{1}H-NMR 中多重峰的精细结构。见图 3-14。

九、C,H 远程核磁共振相关谱（COLOC 或 HMBC）

上述 CHCOSY 技术系采用$^{1}J_{CH}$偶合，解决一键 CH 连接问题，仅回答某碳直接与某氢相连的问题，而不能解决碳与季碳相连的问题，或隔碳相连的问题。改进的 CHCOSY 技术，采用较小的$^{2}J_{CH}$或$^{3}J_{CH}$偶合常数进行调节（通常（2～25）Hz），则可得相隔 2 个或 3 个键的 CH 相关谱，即远程异核化学位移相关谱。由此可解决绕过季碳或杂原子而进行远程的 CH 关联。通常采用两种方法 COLOC 方法和 HMBC 方法，前者用^{13}C检测，灵敏度差，而且可靠性不够；后者系采用^{1}H检测技术，不仅灵敏度高，而且相关信号多，且可靠性强。

图 3-15 为 α-蒎烯的 CHCOLOC 谱（或 HMBC 谱）。从图中可以看出，要确定与季碳 $\delta = 38.0$ 的 CH 联接关系，^{1}H-NMR 中相隔二、三键的质子有 $\delta = 0.85$、1.16 和 1.17 3 个氢。具体分析可从一个质子信号为起点，从其交叉峰信号沿横坐标找出相交的^{13}C信号，此^{13}C信号便是与起点的^{1}H信号相隔二、三个键的 C 原子核。例如 $\delta = 0.85$ 和 1.27 的 CH_3 质子与 $\delta = 38.0$、40.9 和 47.2 的 C 原子相隔二、三个键，见图 3-15 中前两个结构式。由于 CH_3 质子而得到的 CH 相关信号已证明是可靠的；另外超过三键的 CH 相关，反式比顺式易被观察；W 型也易出现。如 $\delta = 1.16$ 与 $\delta = 38.0$，为反式，可看到 CH 相关；而 $\delta = 2.34$ 与 $\delta = 38.0$ 为顺式，则看不到 CH 相关。

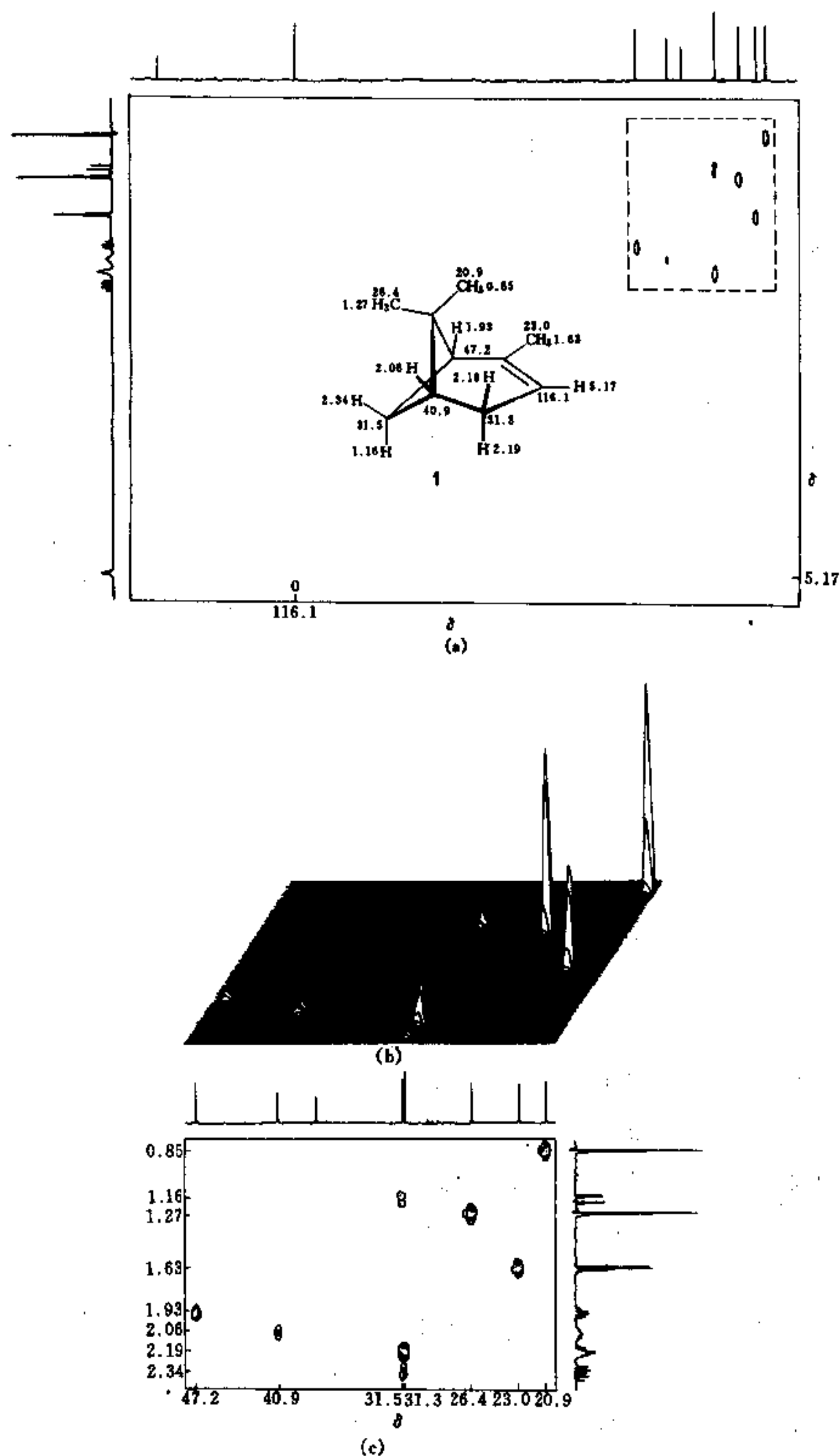


图 3-14　α-蒎烯的 CHCOSY 谱[$(CD_3)_2CO$，$\varphi = 10\%$，25℃，50MHz (^{13}C)，200MHz (^1H)]

(a) 等高线图；(b) 部分的堆形图 [$\delta_C = 20.9 \sim 47.2$；$\delta_H = 0.85 \sim 2.34$]；

(c) 图 b 的等高线图（图中的^1H和^{13}C交叉信号即为相关的 CH）

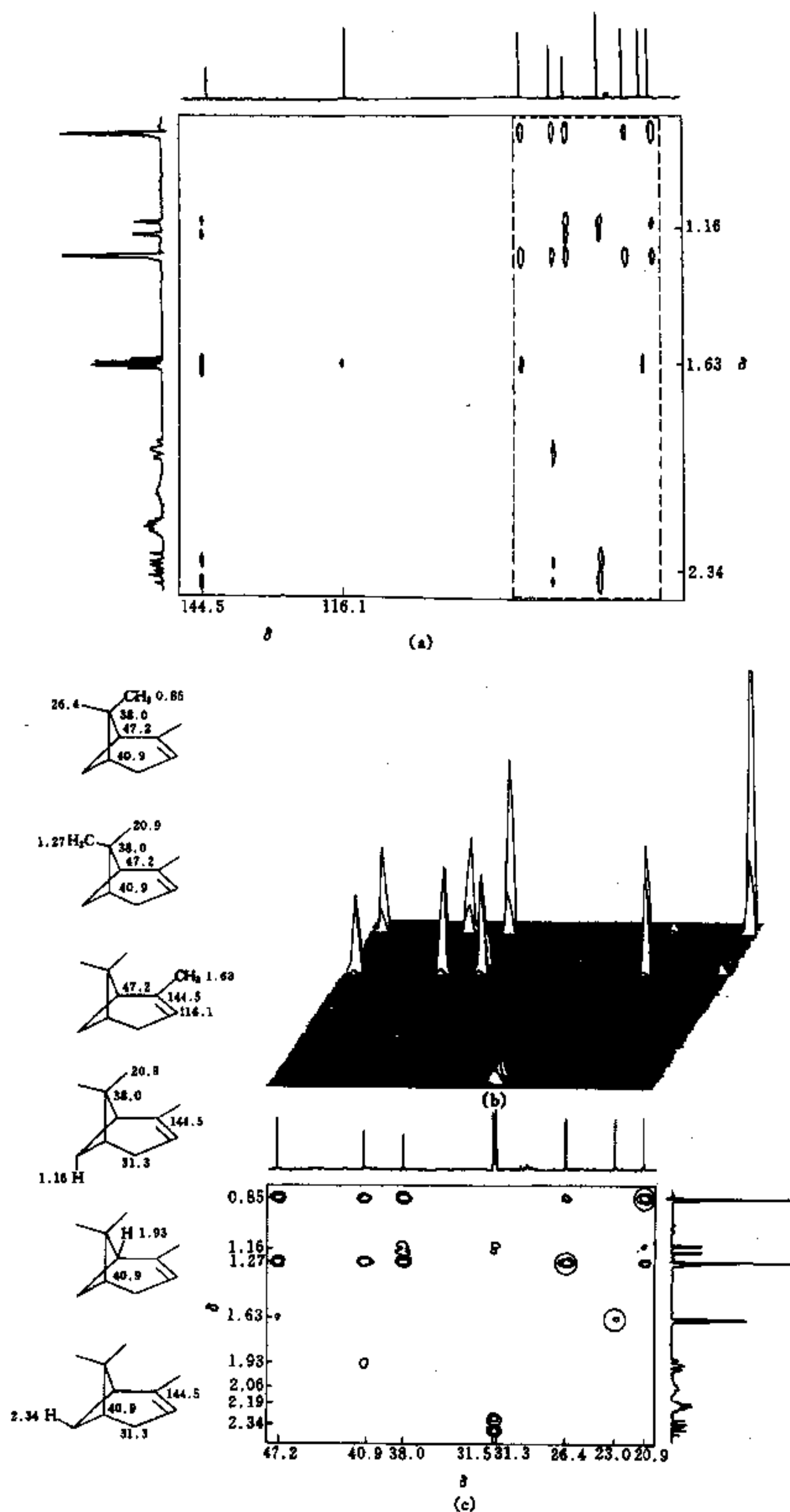


图 3-15　α-蒎烯的 CHCOLOC 谱[$(CD_3)_2CO$，$\varphi=10\%$，25℃，50MHz (^{13}C)，200MHz (^{1}H)]

(a) 等高线图；(b) 部分堆形图 [$\delta=20.9\sim47.2$ (^{13}C) 和 $\delta=0.85-2.34$ (^{1}H)]；

(c) 为图 (b) 的等高线图 (划圈的信号为$^{1}J_{CH}$偶合，难于全部抑制掉)

第三节　相对构型和构象[3,7,8,11]

一、H,H偶合常数

邻位偶合常数$^3J_{HH}$与分子中偶合氢的平面夹角（ϕ）有关，遵守Karplus方程：

$$^3J_{HH}=a\cos^2\phi-0.28\ (\phi<90°,\ a=8.5;\ \phi>90°,\ a=9.5) \quad (3\text{-}1)$$

上述关系亦可用Karplus曲线表示（图3-16），由图看出$\phi=90°$，$^3J_{HH}$最小，$\phi=0°$或180° $^3J_{HH}$最大。电负性取代基可减少$^3J_{HH}$偶合常数。在取代乙烷的稳定构象元13a～c中，*syn*氢$^3J\approx3.5$Hz，*anti*-氢$^3J\approx14$Hz。如果C—C单键自由旋转，则偶合的氢通过*syn*构型两次，通过*anti*构型一次，由方程式：

$$^3J_{平均}=(2J_s+J_a)/3=7\text{Hz} \quad (3\text{-}2)$$

则平均偶合常数为7Hz左右，这是可自由旋转烷基特征的$^3J_{HH}$偶合常数。例如，二溴二氢肉桂酸乙酯(14)，通过α-苯环的C—C单键转动，可生成3种稳定的构象元14a～c。由其^{1}H-NMR(图3-17)谱显示邻位2个氢构成的AB系统，偶合常数$^3J_{AB}=12$Hz。由此可以证明：2个CH键的平面夹角(ϕ)为180°；构象元14b基团间的位阻最小；C—C单键间的转动受阻。由$^3J_{AB}$偶合常数证明氢间的相对构型，同时也证明这部分分子结构的构象。另外，从氧乙基的HH偶合常数(7Hz)也反映出乙基中C—C键的转动不受阻，所有稳定构象元是按比例的。

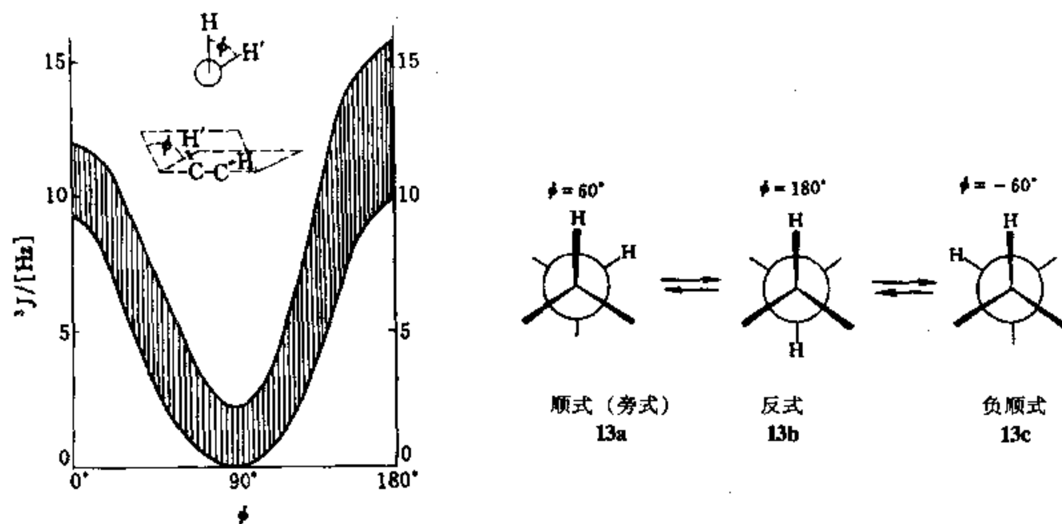
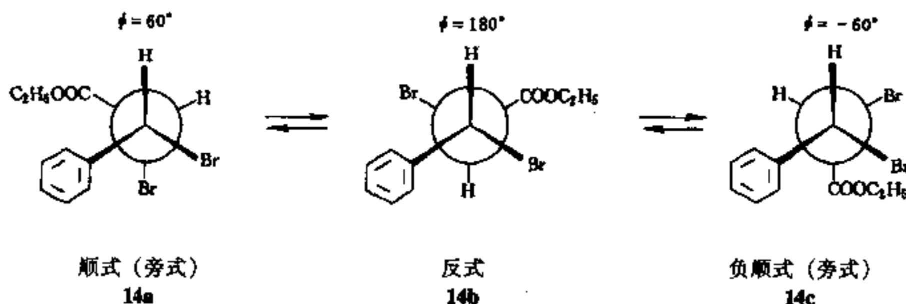


图3-16　邻位偶合常数$^3J_{HH}$和平面夹角的关系（Karplus曲线）



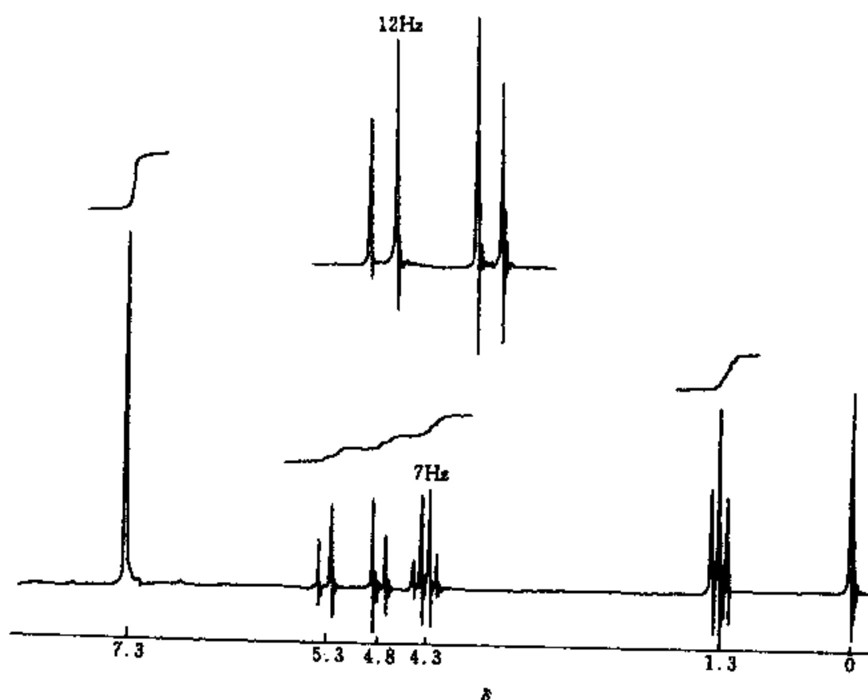


图 3-17　二溴二氢肉桂酸乙酯（14）的^{1}H-NMR 谱（$CDCl_3$，25℃，90MHz）

表 3-10 给出一些刚性系统的$^3J_{HH}$偶合常数，也是符合 Karplus 方程式的。其中环丙烷中$^3J_{HH}$（顺）>$^3J_{HH}$（反），因为顺式氢间 ϕ 为 0°，而反式为 145°。类似地，在环丁烷、环戊烷、降冰片烷和降冰片烯中顺式、内向型和外向型体呈现较大的$^3J_{HH}$偶合常数。

在环状物中，如四元环、五元环和七元环衍生物，取代基的电负性和构型会影响$^3J_{HH}$偶合常数，有时甚至会改变顺-反的$^3J_{HH}$偶合关系，因此必须应用其他的谱学方法，如 NOE 差谱等来证明分子的相对立体化学。但是，$^3J_{HH}$偶合常数对环己烷及其杂环类似物和环己烯的相对构型确定特别有效。环己烷的邻位双直立质子具有大的$^3J_{HH}$偶合常数[$^3J_{aa}$ = (11 ~ 13) Hz]，易于与其他双平展或直立-平展[$^3J_{ee}$ = $^3J_{ae}$ = (2 ~ 4) Hz]$^3J_{HH}$偶合相区别。类似的偶合性质也可在吡喃糖苷中出现，只是由于电负性氧原子的影响减小偶合常数值，使$^3J_{aa}\approx$ 9Hz，$^3J_{ae}\approx$ 4Hz。这对于取代环己烷、环己烯、萜类、黄烷及其糖苷化合物的相对构型确定是很有用的。在这些类型的化合物中，由$^3J_{HH}$证明其相对构型同时亦显示这些六元环的构象。例如，甲基-β-D-吡喃葡萄糖苷（15）的 1-H 和 2-H 其$^3J_{HH}$为 9Hz，不仅可确定偶合氢的双直立构型，而且又证明吡喃糖环为$^4C_1$ 构象。如果是空间较拥挤的$^1C_4$ 构象，1-H 和 2-H 将是双平展型，$^3J_{ee}$应为 4Hz。如果构象元反转，$^4C_1$ 和$^1C_4$ 各占 0.5，则偶合常数应为其平均值 6.5Hz。

1,2-双取代双键化合物的邻位偶合常数，如双氢为顺式（16a）和（17a），$^3J_{HH}$位于(6 ~ 12)Hz 范围，其双平面夹角为 0°；如双氢为反式（16b）和（17b），则$^3J_{HH}$位于(12 ~ 17)Hz 范围，双平面夹角为 180°。这也符合 Karplus 方程式。典型例子如下：

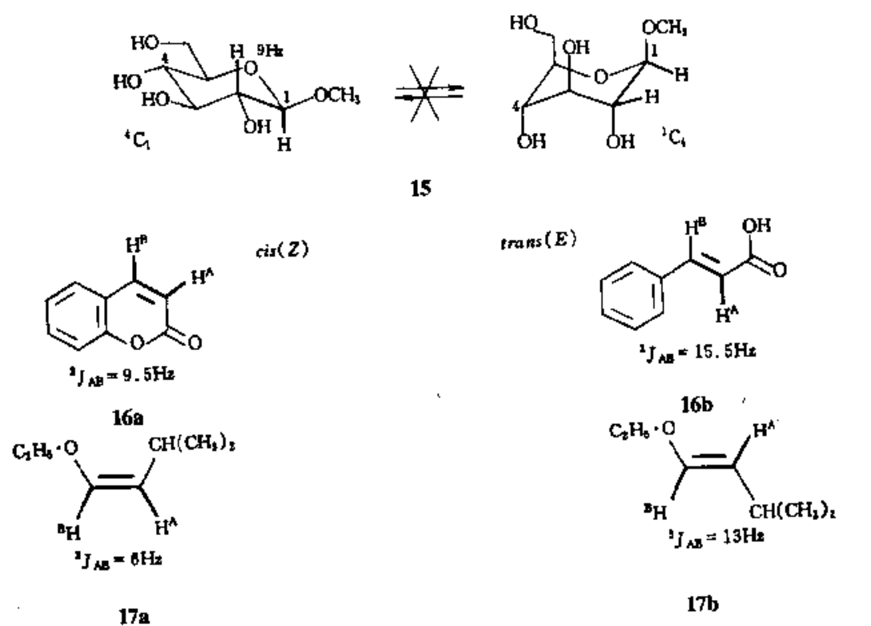
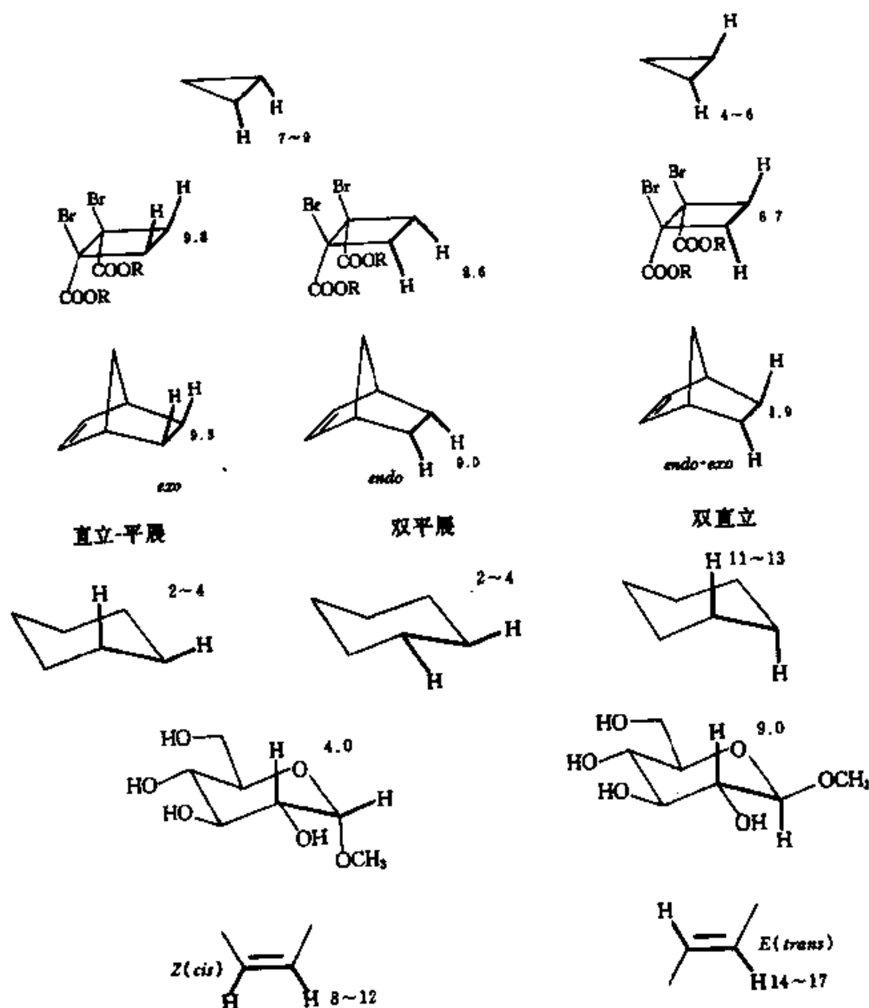


表 3-10　若干典型环系的 $^3J_{HH}$ 偶合常数和相对构型的关系



二、C,H偶合常数

二键的 C,H 偶合常数可鉴定具有明确立体结构分子中电负性取代基的空间取向。如电负性取代基与偶合氢为顺式，其$^2J_{CH}$偶合常数负值增大；反式则$^2J_{CH}$为正值，如 β-和 α-D-吡喃葡萄糖（18a 和 18b）以及溴乙烯（19）。

邻位 CH 偶合常数$^3J_{CH}$类似于$^3J_{HH}$偶合常数与 C—C 键和偶合 C—H 键间的双平面夹角 ϕ 有关，下面用构象元 20a ~ c 的 Newman 投影式加以说明。因为烷基中 C—C 键的自由旋转，使$^3J_{CH}$偶合常数平均化，可预见$^3J_{CH}=(2J_{syn}+J_{anti})/3=4.5\text{Hz}$，所以邻位 CH 偶合常数$^3J_{CH}$大约等于$^3J_{HH}$偶合常数的 0.7 倍。邻位$^3J_{CH}$偶合常数与$^3J_{HH}$偶合常数类似，也能提供环己烷和吡喃糖环以及烯类中 C 和 H 偶合对的相对构型信息取代环己烷中顺式偶合对$^3J_{CH}=(2\sim4)$ Hz、反式$^3J_{CH}=(8\sim9)$Hz,吡喃糖分子中电负性羟基将减小$^3J_{CH}$值。$^3J_{CH}$偶合常数可用来确定多取代烯衍生物的构型。通常反式$^3J_{CH}$ > 顺式$^3J_{CH}$。偶合碳原子上的电负性取代基增加 J 值，而非偶合碳上电负性取代基则减小 J 值。$^3J_{CH}$与碳原子的杂化类型和立体位阻有关。其他典型例子见表 3-11。

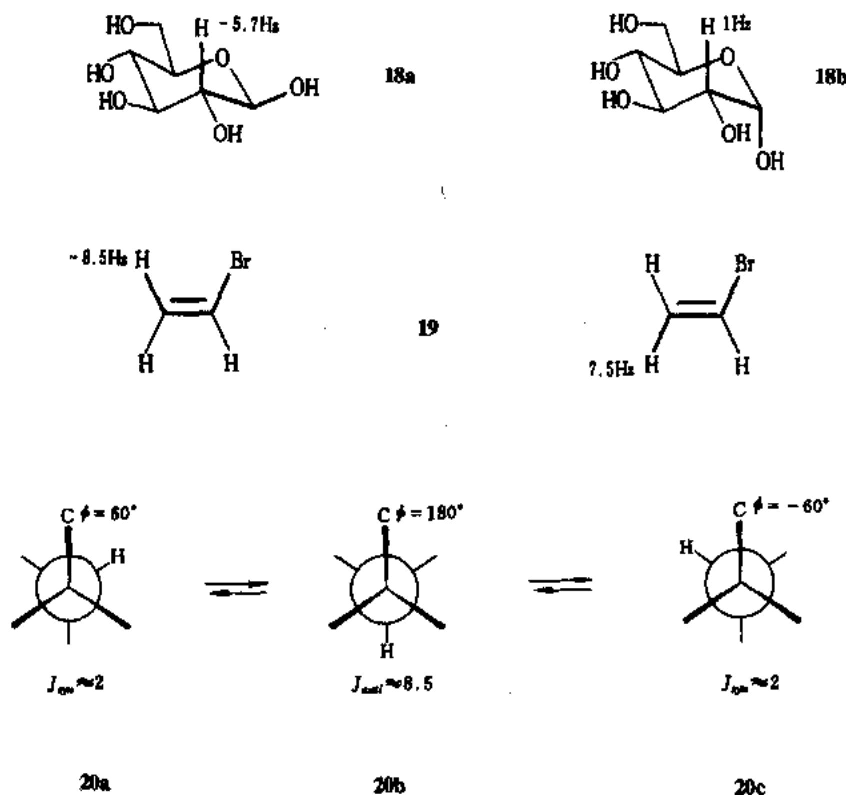


表 3-11　若干典型结构的$^3J_{CH}$偶合常数和相对构型的关系

顺式

Ph Ph Ph O CN H 4.3 H 2.1

HO HO O HO H 0~2 OH OH

反式

8.1 H　9.0 H Ph Ph Ph O CN

HO HO O HO 5~6 H OH OH

顺式

反式

7.5 H CH₃ 12.6 H H　7.8 H 11.9 H　8.1 H 14.7 H CH₃

顺式

反式

9.1 H CH₂Br 15.5 H H　4.6 H CH₃ 8.9 H Br

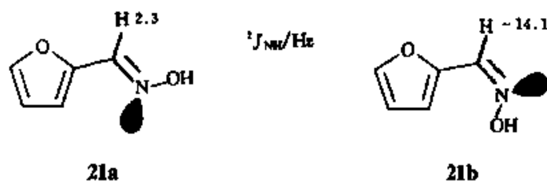
顺式

反式

10.1 H H O 15.9 H H　9.5 H H O 15.1 H CH₃　H CH₃ O 11.0 H CH₃

三、N,H 偶合常数

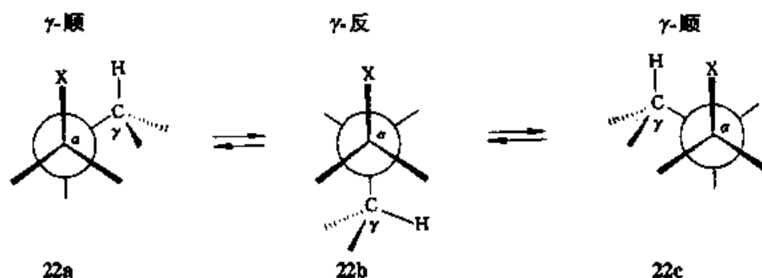
由于$^3J_{NH}<5Hz$，所以$^3J_{NH}$和偶合核间平面夹角的关系很少用来确定立体构型。相反$^2J_{NH}$很易区别醛亚胺的相对构型。例如反式呋喃-2-醛肟（21a）的$^2J_{NH}$值大于顺式异构体（21b），这是由于在亚胺中，未成键电子对与偶合氢是顺式，从而对二键 NH 偶合产生负贡献。



21a　　**21b**

四、^{13}C 化学位移

烷基中的 C 原子受到 γ-位取代基的屏蔽，而导致^{13}C 化学位移值变小，或者说有一个负取代基效应称 γ 效应。γ 效应来源于 CH 键的空间诱导极化作用：即 γ-C 上氢原子和取代基在范德华半径内发生交盖，于是 σ 成键电子从 H 原子移向 γ 碳原子，致使 C 原子的电子密度较高而屏蔽。例如 22a~c 的 Newman 投影式所示 γ-顺式具有强的影响，而 γ-反式则影响较弱。如果存在 C—C 键的自由旋转则产生平均化的结果，即（2γ-顺 + γ-反）/3，从而在烷基衍生物中可观察到高场移动（2.5~3.5）ppm 的 γ 效应。



在刚性分子中，^{13}C化学位移的γ效应，可高达10ppm，据此可鉴定不同构型的异构体。例如顺式和反式3-和4-甲基环己醇(表3-12)，若羟基是直立型，由于其平面氢的范德华作用，

表 3-12　若干环烷，吡喃糖和烯烃的^{13}C-NMR化学位移和相对构型的关系（γ效应）

化合物	相对构型与化学位移	
3-甲基环己醇	顺式：22.5 H_3C，34.8，24.4，34.4，31.7，44.0，70.5，OH	反式：20.2 H_3C，34.4，20.2，32.8，26.6，41.2，66.5，OH
4-甲基环己醇	反式：21.7 H_3C，31.4，31.1，33.1，69.7，OH	顺式：20.9 H_3C，30.6，28.7，31.4，65.9，OH
D-吡喃阿拉伯糖（$^1C_4$ 构象）	α-：67.5，97.4，73.6，69.7，73.1，OH	β-：63.8，93.3，69.9，69.3，69.8，OH
D-吡喃木糖（$^4C_1$-构象）	β-：HO 69.3，65.2，74.1，HO 75.9，96.7，OH	α-：HO 69.5，61.0，71.6，HO 73.0，92.3，OH
2-甲基降莰烷	外型：35.0，H，37.3，30.3，40.2，29.0，43.5，36.8，CH_3 22.3	内型：38.9，38.2，30.6，40.7，22.4，42.2，34.6，H，CH_3 17.4
2-降冰片烷醇	外型：34.6，H，35.8，28.8，42.4，24.9，44.5，74.4，OH	内型：37.8，37.7，30.3，39.6，20.4，43.1，72.5，H，OH
2-己烯	反式：H，34.1 CH_2—CH_2—CH_3（22.1，12.6），123.9，130.6，16.5 CH_3，H	顺式：11.4 CH_3，28.2 CH_2—CH_2—CH_3（21.4，12.5），122.8，129.7，H，H

而导致 γ-C 的屏蔽，化学位移向高场移动。在环己烷，降冰片烷和吡喃糖分子中，取代基和氢原子间的1,3 -双直立关系而屏蔽所涉及的 C 原子产生比平展型异构体小的^{13}C 化学位移值。

所以，在已知构象的分子中，^{13}C 化学位移可确定分子中取代基的相对构型。例如在反式-3-甲基环己醇，顺式-4-甲基环己醇，β-D-呋喃阿拉伯糖和 α-D-吡喃木糖中羟基的直立取向。另外也可推导出这些化合物具有一定的构象（表 3-12 中，吡喃阿拉伯糖为$^1C_4$；其他为$^4C_1$ 构象）。如果它们以别的构象元存在，则分子中的 C-1 羟基必是平展型，C-1，C-3 和 C-5 有较大的化学位移。如环反转则产生平均化的^{13}C 化学位移（两者构象元各占 50%）。

同^{1}H 化学位移相比，^{13}C 化学位移对立体效应比较敏感，图 3-18 给出顺式和反式 4-叔丁基

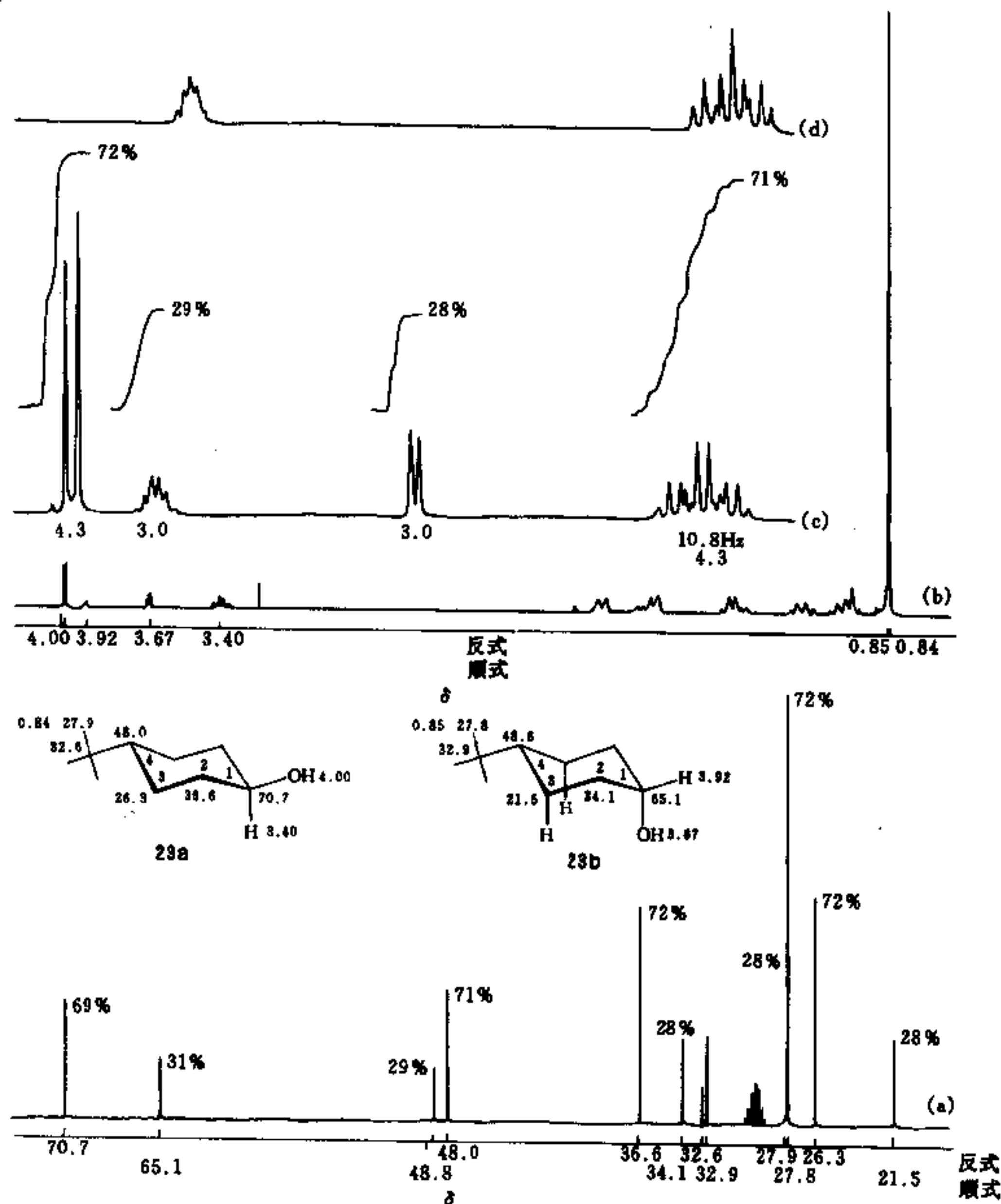


图 3-18 反式和顺式-4-叔丁基环己醇（23a 和 23b）的 NMR 谱

[$(CD_3)_2CO$，25℃，400MHz (^{1}H)，100MHz (^{13}C)]

(a) 氢宽带去偶^{13}C-NMR 谱；(b)^{1}H-NMR 谱；(c) 为 (b) 谱 δ= (3～4) 的放大图；(d) 为 D_2O 交换的 (c) 图

环己醇(23)的^{1}H 和^{13}C-NMR 谱的比较。顺式异构体(23b)直立羟基通过 γ-CH 键空间的极化作用而使 C-1 的化学位移向高场位移 5.6 个单位,使 C-3 化学位移向高场移 4.8 个单位(γ 效应)。相反地,^{1}H 化学位移在环己烷键中仅表现相当小的各向异性效应,平展型取代基(在 H 和 OH 情况下)比直立型取代基具有较大的化学位移;顺式-23 平展型 1-H($\delta = 3.92$)比反式-23 直立型 1-H($\delta = 3.40$)的化学位移值大,差值为 0.52 个单位,比 γ 效应使^{13}C 化学位移的高场移动(一般为 5 个单位)重要性要差得多。但是将二者结合起来,通过测量积分面积或信号强度可对混合物进行定量分析,表现出 NMR 谱在定量分析方面的重要价值。

图 3-18 为反式和顺式-4-叔丁基环己醇的 NMR 图。由图3-18(c)的积分和图 3-18(a)强度得出反式:顺式异构体比率为 71:29。反式异构体 23a 中的 1-H（$\delta = 3.40$）呈现一个四重峰的三重峰（2 个反向2,2′-H，$J = 10.8$Hz；两个顺向2,2′-H，$J = 4.3$Hz；另一个偶合对 OH)。当 D_2O 交换后则呈现 1 个三重峰（4.3Hz）的三重峰（10.8Hz），而消除 OH 的偶合。在顺式异构 23b 中 1-H（$\delta = 3.92$）呈现 1 个六重峰（2,2′位的 4 个顺向氢和 OH，$J = 3.0$Hz），D_2O 交换后则变成五重峰。

在^{1}H-NMR 中通过 D_2O 交换消除由 OH 而产生的偶合，可由图3-18(d)加以说明。

γ 效应对^{13}C 化学位移的影响能够鉴别烯烃取代基的 E-和 Z-构型。这里 α-C 的位移变化明确反映双键构型改变；在顺式烷基中的 α-C 原子处于相关核的 γ 位置，双平面夹角为 0°，从而产生特别强的范德华相互作用，导致相应^{13}C 核强的屏蔽,^{13}C 化学位移处于明显高场。因此，对烯烃的 α-C 原子 $\delta_{反} > \delta_{顺}$，见表 3-12 中（E）和（Z）-2-己烯。

α，β-不饱和羰基的^{13}C 化学位移值比饱和羰基的值小，说明前者的羰基和双键共平面。如存在空间位阻而防碍共平面，则共轭性降低,^{13}C 化学位移值增大。例如，在苯甲酸衍生物(24）中，若羰基双键和其他 π 系统间的平面夹角不同，可由^{13}C 化学位移反映出来，并由此可推导出它们的构象。具体数据如下：

24

R	$\delta_{C=O}$	$\theta/(°)$
H	166.9	0
CH_3	170.4	49
$CH(CH_3)_2$	171.3	57
$C(CH_3)_3$	173.1	90

五、NOE 差谱

核自旋去偶引起信号强度的改变称核欧沃豪斯效应（NOE)。氢去偶的^{13}C-NMR 谱，由于 NOE 增加连氢碳原子的信号强度，有的高达 200%。在^{1}H-NMR 谱中，由 NOE 引起的氢信号强度增益比^{13}C-NMR 中要小得多，最多增益为 50%。

NOE 对确定构型是很有效的。NOE 增益是通过空间作用而不是通过化学键而完成的。只要分子中两个核相距较近，一般不超过 0.3nm，若对其一去偶，则另一核可产生 NOE 变化。因此，分子的运动，核的偶极弛豫过程及核的能级布居改变均能影响 NOE 效果，从而影响信号强度变化。所以，如果一个氢信号强度由于另一个氢核的去偶而增加，则这些氢核必须是相互靠近的，而与它们相隔的化学键数目无关。

NOE 差谱是一种研究分子中氢原子空间距离靠近的有效方法。在实验中，记录^{1}H-NMR 谱的同时，去偶另一个特定的氢核，使之与该去偶氢核靠近的氢信号产生 NOE 增益（测量

1)；另外测一个偏共振的[1]H-NMR 谱（测量 2），测量 1 减去测量 2 即得到 NOE 差谱，从中可看出强度增加的信号（正 NOE）或强度减弱的信号（负 NOE）。NOE 差谱可提高普通 NOE 谱的灵敏度，准确性高。图 3-19 为 α 蒎烯（1）的 NOE 差谱，去偶 $\delta=1.27$ 的甲基质子，$\delta=2.34$ 的氢产生明显的 NOE 增益。为进一步证明，可去偶 $\delta=0.85$ 的甲基质子，此时 $\delta=2.34$ 的信号不产生 NOE 增益。由此说明 α-蒎烯分子中 $\delta=2.34$ 的质子空间靠近 $\delta=1.27$ 的甲基，而远离 $\delta=0.85$ 的甲基。另外，此实验也可对分子中 $\delta=0.85$ 和 1.27 两个甲基信号进行归属。图中在 $\delta=1.16$ 产生负信号。这是由于 $\delta=2.34$ 同碳氢偶合作用的结果。

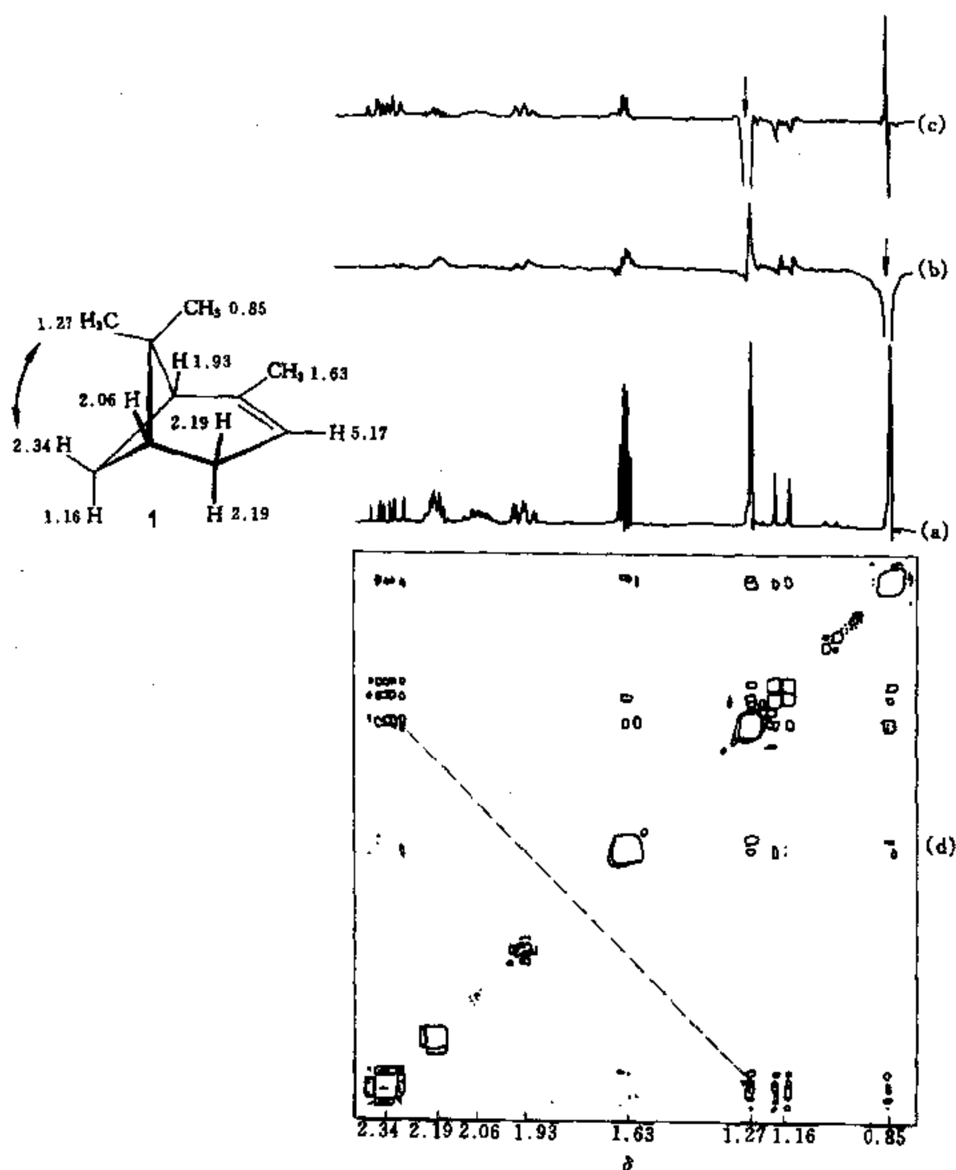


图 3-19　α-蒎烯的[1]H-NMR 谱（a），HH-NOE 差谱（b），（c）和 HH-NOESY 谱（d）的比较
[$(CD_3)_2CO$, $\varphi=10\%$，25℃，200MHz，取其 $\delta=0.85\sim2.34$]

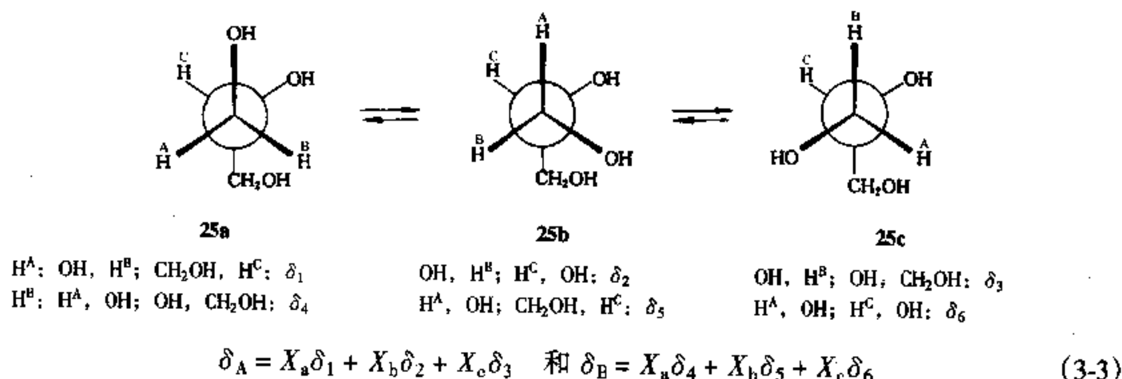
六、HH-NOESY 谱

HH-COSY 谱可确定分子中 HH 连接问题。而 HH-COSY 谱的脉冲序列又可同时改变能级的布居分配，而导致 NOE。因此，为得到信号强度改变的二维实验即 NOESY 谱，可将 HH-COSY脉冲序列扩展为 HH-NOESY 脉冲序列。图3-19(d)为 HH-NOESY 谱。HH-NOESY 谱的图形与 HH-COSY 谱相同，同时二者图的分析方法也类似。只是图中的相关交叉信息不是通过化学键的相互偶合关系，而是通过空间相互靠近的 NOE 关系。例如在 $\delta=2.34$ 和 1.27 的交叉信号说明 α-蒎烯分子中此处氢空间相互靠近。要注意的是，HH-NOESY 谱中往往残留一些 HH-COSY 谱的信息。因此，在进行 HH-NOESY 谱测量之前，最好先测 HH-COSY 谱，二者比较则可得到较精确的 NOE 结果。比较两种测 NOE 的方法，即 NOE 差谱和 NOESY 谱，HH-NOE 差谱更好，省时、选择性高且较准确。

第四节　绝对构型[3,9,10]

一、非对映异构作用

CH_2 中的二个氢原子经过转动或其他对称性移动，二者不能处于化学上相同的位置，称为非对映异构的（diastereotopic)。非对映异构的精确意义可用甘油中 2 个亚甲基质子 H_A 和 H_B 说明。若沿 C—C 单键旋转，末端 CH_2OH 基团可转动成 3 个稳定构象，用 Newman 投影式表示如下：25a ~ c，其中 CH_2 质子 H_A 和 H_B 的化学环境是不同的，可从 6 种可能的构象元加以区别。如果停止旋转，则每种构象元 a，b 和 c 中 H_A 和 H_B 各有 3 种不同的化学位移：H_A 有 δ_1、δ_2 和 δ_3，H_B 有 δ_4、δ_5 和 δ_6，若在常温自由旋转，并设 X_a，X_b 和 X_c 分别是构象 a，b 和 c 的布居数，则可根据方程式（3-3）计算 H_A 和 H_B 的化学位移。



$$\delta_A = X_a\delta_1 + X_b\delta_2 + X_c\delta_3 \quad 和 \quad \delta_B = X_a\delta_4 + X_b\delta_5 + X_c\delta_6 \tag{3-3}$$

如测出的平均化学位移 $\delta_A \neq \delta_B$ 则表示即使所有 3 种构象存在等量的数目（$X_a = X_b = X_c = 1/3$)，δ_A 和 δ_B 也是不同的。H_A 和 H_B 的化学等价必须是它们的化学环境完全相同，图 3-20 给出甘油中亚甲基质子（CH_AH_BOH）的非对映异构作用（diastereotopism)；其中 $\delta_B-\delta_A=0.09$。^1H-NMR 谱显示一个对称的（$(AB)_2C$ 系统，$(CH_AH_BOH)_2$-CH_COH，其同碳偶合常数$^2J_{AB}=11.6$Hz，邻位偶合常数$^3J_{AC}=6.4$Hz 和$^3J_{BC}=4.5$Hz。不同的^3J 偶合说明甘油中 C—C 键无受阻而自由转动。并指出构象 a 或 c 比 b 占优势，因其取代基间的作用弱。

非对映异构作用显示原手性（Prochirality)，如甘油及其他例子（如二乙基缩乙醛），其

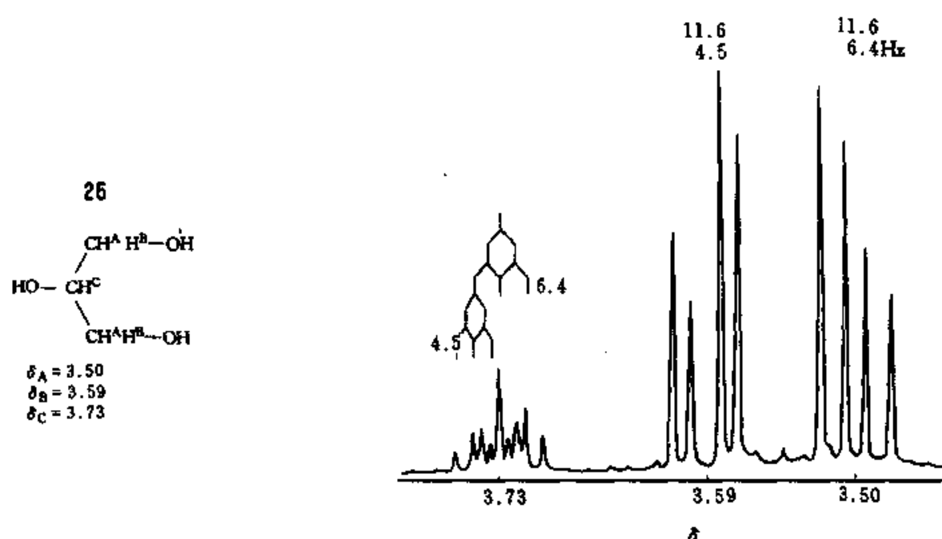
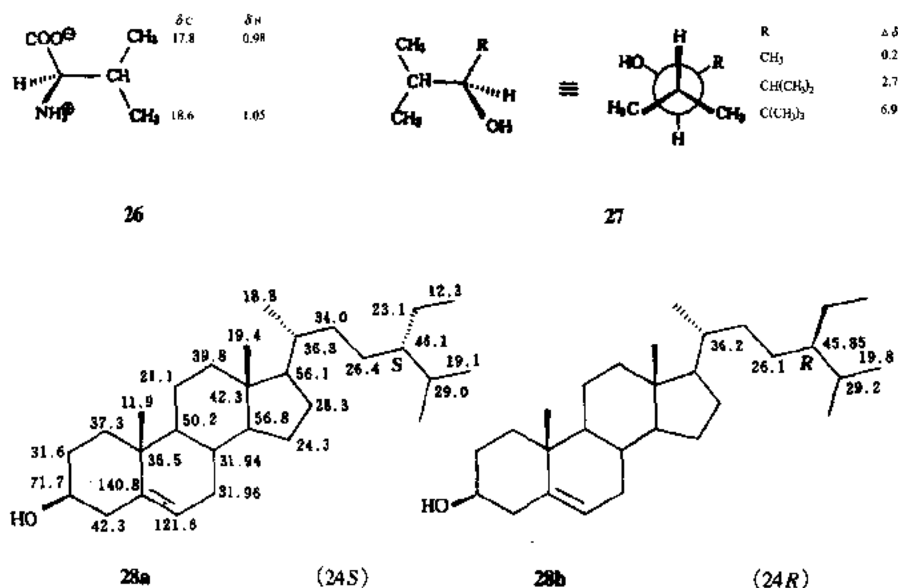


图 3-20　甘油（25）的^{1}H-NMR 谱（D_2O，10%，25℃，400MHz）

中 OCH_2 质子是非对映异构的，属于原手性缩醛 C 原子，因此显示四重峰的 AB 系统（因与甲基质子偶合）。

Newman 投影式 25a～c 中的中心碳原子，从 CH_2—OH 基观察是不对称的，也是非对映异构的。在 L-缬氨酸（26）分子中异丙基的甲基也是非对映异构的，所以呈现不同的^{1}H 和^{13}C 化学位移。在手性醇（27）分子中，异丙基碳的非对映异构性随烷基的大小而增加（甲基 < 异丙基 < 叔丁基）。

如果一个分子含几个不对称碳原子，则每个非对映异构体呈现其本身的非对映异构的化学位移。例如，穿贝海绵甾醇（28a）和谷甾醇（28b）是两个甾体化合物，其区别仅是 C-24 的绝对构型不同。在 28a 和 28b 中，靠近不对称碳原子的^{13}C 核呈现不同的^{13}C 化学位移，以此可对二者进行鉴别，包括对 C-24 绝对构型的鉴定。吡咯里西啶酯类生物碱分子中羧酸的绝对构型亦可由其非对映异构的^{1}H 和^{13}C 化学位移表现出来。



二、手性位移试剂（*ee* 值测定）

分子中存在不对称碳原子，常常可通过其非对映异构体的化学位移加以鉴定，而且可通过比较其非对映异构体的化学位移来测定其绝对构型。但是用 NMR 方法不能鉴别对映体，NMR 谱不能证明手性化合物是以外消旋体形式存在还是纯的对映体。

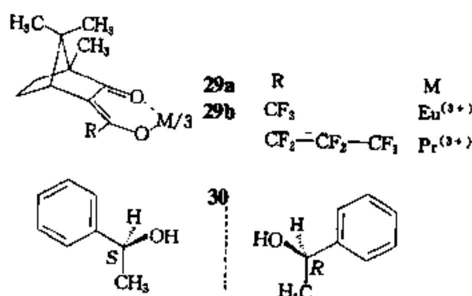
然而，可用一个手性试剂转变外消旋体为非对映异构体，或者可采用更简便方法，将样品溶解在对映体纯的溶剂 R 和 S 中，生成样品（P）的溶剂化外消旋体（R:RP 和 P:SP），此为非对映异构体，具有不同的化学位移，借此可以鉴别对映体。分子中若含有由于各向异性效应而影响化学位移的基团，更适合于用手性溶剂加以鉴别。例如，1-苯乙胺和2,2,2-三氟-1-苯乙醇。

用 NMR 谱测定对映体纯度的可靠方法是手性位移试剂法。常用铕（Ⅲ）或镨（Ⅲ）络合物（29）为手性位移试剂，与外消旋样品生成非对映异构的铕（Ⅲ）或镨（Ⅲ）的络合物，二者具有不同的化学位移，其中靠近活泼基团（OH，NH_2，C═O）的核更能呈现不同位移的信号，信号的分离程度随位移试剂浓度的增加而加大。但是由于顺磁性离子的增加而导致信号加宽，限制了位移试剂的用量。对映体过量（*ee*）的测定可用下式计算：

$$ee = \frac{R-S}{R+S} \times 100\% \qquad (3\text{-}4)$$

式中，*R*、*S* 分别表示样品中 *R* 构型和 *S* 构型的量。

用手性位移试剂，*tri*[3-(heptafluoropropylhydroxy methylene)-D-camphorato]praseodymium(Ⅲ)(29b)测定 1-苯乙醇的 *ee* 值，其^{1}H 和^{13}C-NMR 谱见图 3-21。(a) 和 (b) 是 400MHz ^{1}H-NMR 谱，其中 (a)、(c) 不加位移试剂，(b) 加入位移试剂；在^{13}C-NMR 谱 (d) 中，仅仅对映体 30*R* 和 30*S* 的 α-碳原子信号被分开。苯环的^{1}H 和^{13}C 信号不受影响，图中未表示。由积分面积计算 *R* 型占 73%；*S* 型占 27%，所以对映体过量（*ee*）是 46%。



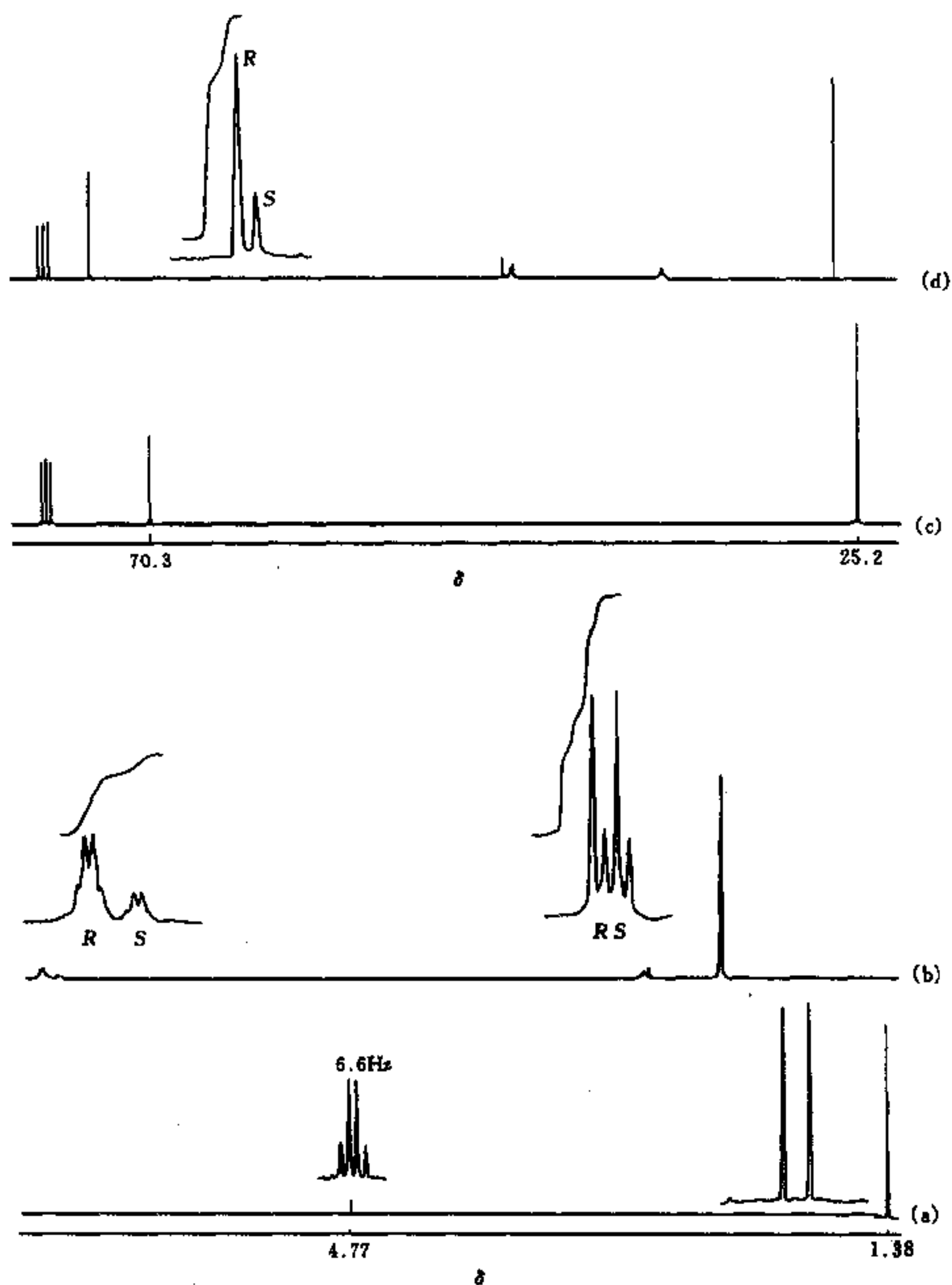


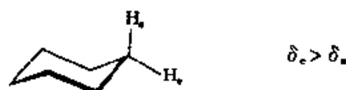
图 3-21 1-苯乙醇（30）对映体过量测定（0.1mmol 试样在 0.3ml $CDCl_3$ 中，加入手性位移试剂（29b）0.1mmol）

第五节 分子内和分子间的相互作用[2,3,11]

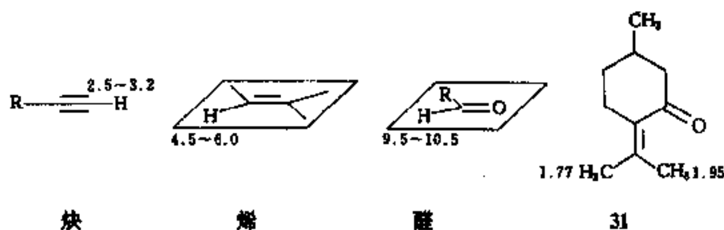
一、各向异性效应

一个核的化学位移部分地受到分子中某个化学键或键系统空间位置的影响，称各向异性效应。这种各向异性效应概念在结构测定中是很重要的。例如环己烷中的直立键氢比其同样

位置的平展型氢总是具有较小的^{1}H 化学位移。^{13}C-NMR 中的 γ 效应也使^{13}C 核具有类似的性质。



多重键体系表现出明显的各向异性，例如双键包括 C═C 和 C═O，其平面为去屏蔽，平面的上方或下方为屏蔽。炔键的两端为屏蔽，而其外周则去屏蔽。例如，用羰基的各向异性效应可区别长叶薄荷酮（31）分子中双键上的甲基。



二、芳香化合物的环电流

苯环的^{1}H 化学位移（$\delta = 7.28$）比烯烃的^{1}H 化学位移，如环己烯（$\delta = 5.59$），大得多，这是由于苯环 π-电子环电流的作用，致使苯环氢去屏蔽的结果。当芳香化合物受到磁场作用时产生环电流，环电流的磁力线有方向性，在环的上下方或环内与外磁场方向相反，在环外与其平行（图 3-22）。因此，处于芳环的上下方或环内的核是屏蔽的，具有小的化学位移；而处于芳环外与芳环共平面的核则是去屏蔽的，呈现大的化学位移。环电流对^{1}H 核的影响要比对^{13}C 核的影响大得多，所以特殊的^{1}H 化学位移对研究芳香性的环电流是一种有效的方法。例如，1,4-十亚甲基苯（32）分子中一些 CH_2 质子位于芳环平面的上方而屏蔽，呈现小的化学位移。在化合物（33）分子中，环中间的质子处于明显高场，而环外质子则处于明显低场。类似例子还有化合物（34）和（35）等。

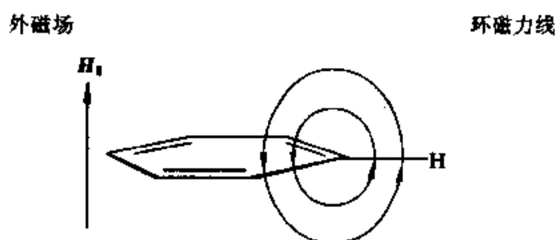
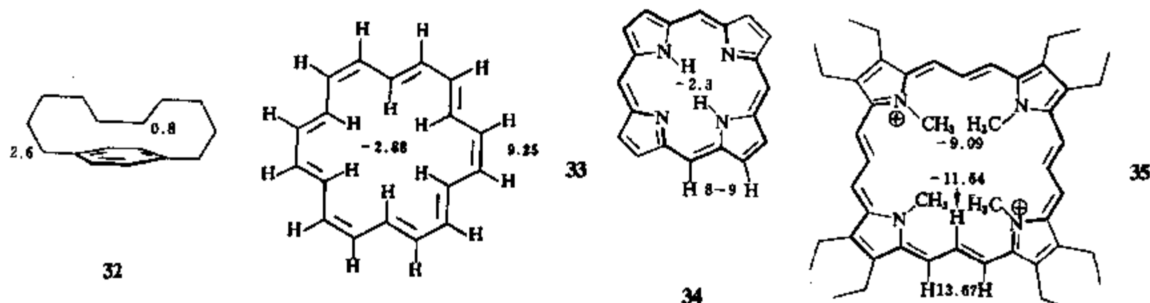


图 3-22　苯环的环磁力线示意图



三、分子内和分子间的氢键

在^{1}H-NMR谱中生成氢键的活泼氢，由于电负性杂原子对氢原子的影响，其化学位移明显向低场移动，由此可辨认氢键。1,3-双酮烯醇式的OH氢是典型例子。它们生成分子内氢键并在$\delta=12.5$（六氟乙酰丙酮烯醇，图3-23）和$\delta=15.5$（乙酰丙酮烯醇）呈现信号。

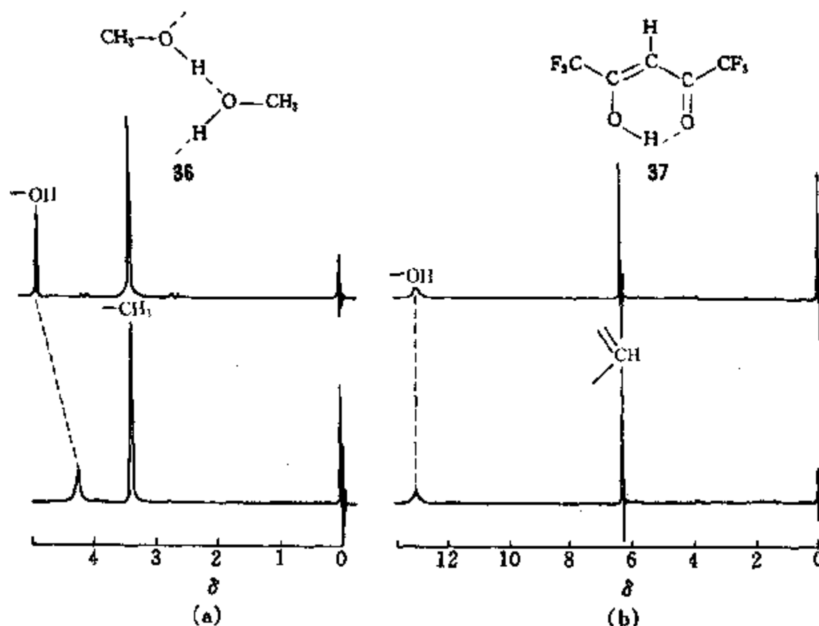


图3-23 纯甲醇（a）和六氟乙酰丙酮（b）的^{1}H-NMR谱（25℃，90HMz）

来源于分子间氢键的^{1}H化学位移受浓度的影响很大，若用溶剂进行稀释，则OH位移按比例减小。相反，分子内氢键的^{1}H化学位移则不受浓度的影响，如图3-22。分子间氢键包括两个不同分子中2个杂原子和氢之间的交换。氢原子不能保留在同一分子中，而是互相交换。如果交换频率大于海森堡测不准原理（方程式3-5）所给出的频率，则其偶合常数J_{AX}对其邻位质子H_A是不能分辨的。因此CH_n质子在常温不被邻位SH，OH或NH质子所裂分。同样情况也适于$^{3}J_{CH}$偶合。

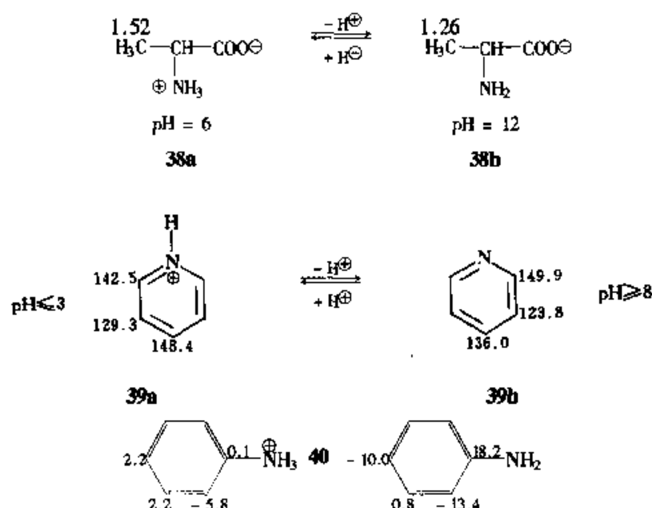
$$\nu_{交换} \geqslant \pi J_{AX}/\sqrt{2} \approx 2.22 J_{AX} \quad (3\text{-}5)$$

若氢键是分子内的，则能测出偶合常数，见前所述的水杨醛（10）的例子。

四、质子化效应

如样品中含有能得到质子或失去质子的基团，如NH_2或CO_2H，测定时的pH和浓度会影响分子中某些基团的化学位移值。例如，丙氨酸（38）在中性（内盐式38a）或碱性（阴离子式，38b）溶液中，分子中的甲基^{1}H-NMR化学位移不同。根据化学位移与pH的依赖关系，由滴定曲线的转折点可测定平衡液中的pK值。

^{13}C化学位移对pH变化的影响更为敏感，例如吡啶（39b）及其正离子（39a）。



苯胺（40）在酸性条件，其^{13}C化学位移和苯胺本身的^{13}C化学位移与苯（$\delta = 128.5$）比亦有明显差异。

第六节　分子动力学[2,3,12]

一、变温 NMR 谱

图 3-24 指出N,N-二甲基乙酰胺的^{1}H-NMR谱与温度的关系。在55℃或低一些的温度，2个N-甲基呈现2个共振峰；在高于55℃则信号加宽直到消失，至80℃形成一个宽峰。该温度称聚结温度（coalescence temperature）T_c，高于T_c，2个N-甲基信号变成尖峰。2个N-甲基信号的改变来源于酰胺基团C—N键的部分双键化，从而阻碍N,N-二甲胺基团的转动，使其一个甲基与酰胺氧为顺式（$\delta_B = 3.0$），而另一个为反式（$\delta_A = 2.9$）。在低于55℃时，分子中N-甲基质子慢慢交换位置（慢慢旋转，慢慢交换）。若增加能量加热到90℃以上，则N,N-二甲氨基旋转加快，N-甲基质子高频交换位置（自由旋转，快速交换），形成一个单尖峰N-甲基信号，信号强度加倍，平均化学位移$(\delta_A + \delta_B)/2 = 2.95$。

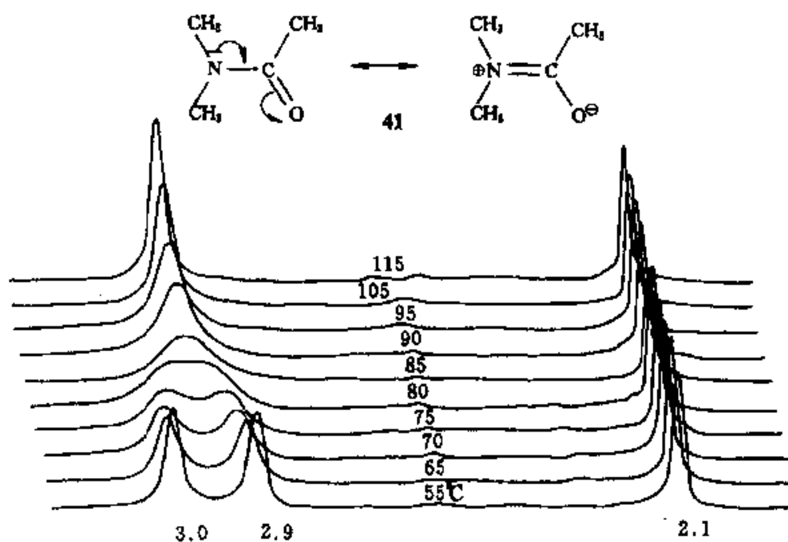


图 3-24　N,N-二甲基乙酰胺（41）在不同温度下的^{1}H-NMR谱
（$(CD_3)_2SO$，$\varphi = 75\%$，100MHz）

二甲氨基旋转服从一级速率规律，交换的甲基质子不发生偶合，形成单一信号。此时在聚结点 T_c 的速率常数 k_r 可由方程式（3-6）求出。

$$k_r = \pi(\nu_B - \nu_A)/\sqrt{2} = \pi\Delta\nu/\sqrt{2} \approx 2.22\Delta\nu \qquad (3\text{-}6)$$

$\Delta\nu$ 是聚结点 T_c 时最大信号的宽度，相当于在慢速交换时化学位移差（$\nu_B - \nu_A$）。以二甲乙酰胺（41）为例，化学位移差是 0.1（图 3-24），即 8Hz（在 80MHz）。从方程式（3-6）计算，在聚结点 80℃（或 353K）N-甲基旋转频率 $k_r = 2.22 \times 8 \approx 17.8$Hz。根据方程式（3-7），交换频率 K_r 与自由分子活化熵 ΔG 成指数衰减。

$$k_r = \frac{kT_c}{h} e^{-\Delta G/RT_c} \qquad (3\text{-}7)$$

R 是气体常数，k 是 Boltzman 常数，h 是 Planck 常数，方程式（3-6）和（3-7）说明变温 NMR 对分子动力学研究的重要价值。经过一些基本常数的变换可得到方程式（3-8）以计算自由分子活化能 ΔG（free molar activation enthalpy），此亦属于一级速率交换过程。

$$\Delta G = 19.1\,T_c[10.32 + \log(T_c/k_r)] \times 10^{-3} \quad \text{kJ·mol}^{-1} \qquad (3\text{-}8)$$

由此，在二甲乙酰胺中，二甲氨基在聚结点 353K 的旋转活化能垒，由方程式（3-8）计算 $k_r = 17.8\text{s}^{-1}$。

$$\Delta G_{353} = 78.5\ \text{kJ·mol}^{-1}\ （或\ 18.7\text{kcal·mol}^{-1}）$$

变温（动力学）NMR 谱，适合于对 10^{-1}和 10^3s^{-1}之间速率常数过程的研究。一些具体例子见表 3-13。

表 3-13　若干动力学^{1}H-NMR 实例

类型	T_c/K	ΔG_{T_c}/kJ·mol^{-1}
旋转受阻	147	30
氮基电子转向	380	80
环转型	193	25
结构互变	298	3

二、^{13}C 自旋晶格弛豫时间

将样品中特定的核自旋集中起来，使之具有平行于外磁场 $\boldsymbol{H}_0$ 方向的时间称自旋晶格弛豫时间 T_1。样品的磁化量 M_0 在每次激发后需在 T_1 时间内进行复原。对有机分子中各种不同键的质子，在溶液中 T_1 具有相同的量级（0.1～10s）。^{13}C 核则不同，核间有较大的差别，与分子的大小及化学环境等有关。^{13}C 核的 T_1 范围较大，从几毫秒（大分子）到几分钟（小分子中的季碳）。因此，在进行氢宽带去偶时对所有碳核仅用一个 T_1 值（而不是用 nT_1 值对^{1}H 多重峰中的 n 条线）。所以^{13}C 自旋晶格弛豫时间通常是做为一种探测溶液中分子流动

性的参数。

测量 T_1 的技术最简单的方法是反转回复法，即采用一种适当的 180° 脉冲反转核自旋分布。开始呈现负信号，随时间延长即增加 T_1 弛豫时间而变成正信号，直至最后达到平衡强度。图 3-25 和 3-26 分别给出两个样品的 ^{13}C 信号振幅，由于 ^{13}C 自旋晶格弛豫时间增加而变化的情况。为简单起见，不考虑标准偏差，而采用信号强度 0 为 T_0 法，由公式（3-9）求出各个 C 原子的 T_1。

$$T_1 = \tau_0/\ln 2 \approx 1.45\tau_0 \tag{3-9}$$

例如图 3-25 给出 2-羟基辛醇（42）分子的 T_1 测量，其中对疏水端的甲基，τ_0 为 3.8s，由方程式（3-9）求出，其 $T_1 = 5.5$s。但实际上，该甲基如完全弛豫约需要再延长 5 倍的时间，即 30s 左右。T_1 是指数变化的时间常数，换句话说在 T_1 之后，所观察到的信号强度和其最终值之差，仍是最终振幅的 1/e。

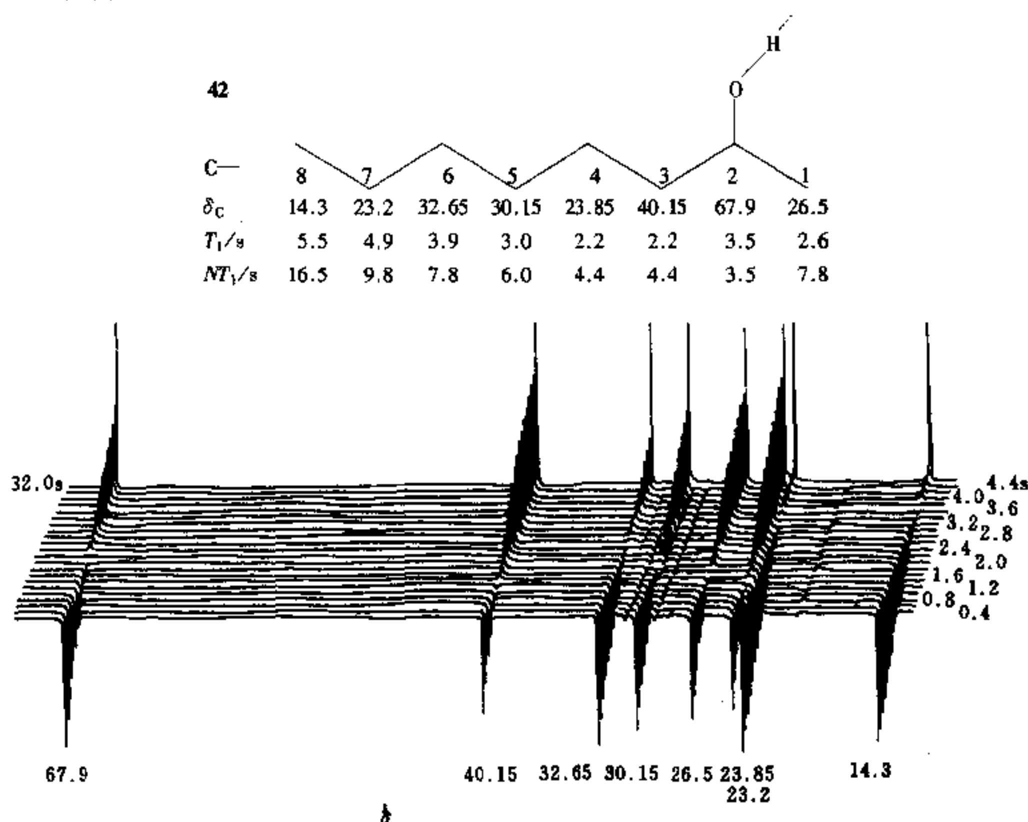


图 3-25 2-辛醇（42）的 ^{13}C 自旋晶格弛豫时间测定序列

（$(CD_3)_2CO$，$\varphi = 75\%$，25℃，50MHz）

NT_1——分子内柔动性参数，N 为碳连氢数目

连氢 ^{13}C 的自旋晶格弛豫是通过偶极-偶极相互作用(DD 机制，偶极弛豫)完成的。对于这样的 ^{13}C 核，当氢宽带去偶时，信号强度的 NOE 增益约为 2 倍，可由方程式(3-10)求出。

$$\eta_c = \gamma_H/2\gamma_C = 1.988 \tag{3-10}$$

其中 γ_H 和 γ_C 分别是 ^1H 和 ^{13}C 核的磁旋比。

若某些 ^{13}C 核的 NOE 增益小，则可能通过其他机制完成自旋晶格弛豫（如自旋-转动）。^{13}C 核的偶极弛豫来源于同分子或邻近分子中氢原子的振动，转动和平移所产生的局部波动磁场。

如果局部波动磁场的频率与^{13}C核的拉莫频率相匹配，则这些核便发生能量转换，从激发态弛豫到基态或者相反由基态到激发态。所以自旋晶格弛豫是与分子或分子片段的运动有关。若将两个分子或其片段之间改变取向所需的平均时间以相关时间 τ_C 表示，而且所观察的 C 原子连有 nH 原子，则偶极弛豫时间 T_1(DD)可用相关函数(3-11)表示。

$$T_1(\mathrm{DD})^{-1} = 常数 \times n\tau_C \tag{3-11}$$

因此，含 H 数目少的 C 原子，其弛豫时间增加，分子或分子片段的运动加快。所以^{13}C的自旋晶格弛豫时间能提供分子中下列四方面的信息。

(1) 分子大小　小分子移动比大分子快，因此，小分子中的 C 原子比大分子中的 C 原子弛豫地慢。例如，环已烷中 C 原子的 T_1(19~20s)比十氢萘的 T_1(4~5s)大得多。

(2) 碳原子结合 H 原子的数目　若分子中所有部分移动速度相同（所有 C 原子的 τ_C 相同)，则弛豫时间 T_1 由 CH、CH_2 至 CH_3 按比例减少，符合方程式 (3-12)。

$$T_1(\mathrm{CH}):T_1(\mathrm{CH_2}):T_1(\mathrm{CH_3}) = 6:3:2 \tag{3-12}$$

由于甲基在任何刚性分子中均可自由旋转，所以在 (3-12) 式中所给出的比率关系仅适用于立体位阻相当大的分子。相反，不管在大分子或刚性分子中，CH 和 CH_2 ^{13}C 核的 T_1 比率关系 2:1 都是适用的。典型例子是甾体化合物 (43)，其环中的 CH_2 比 CH 碳原子弛豫地快 2 倍，CH_2(T_1 = 0.2~0.3s),CH(T_1 ≈ 0.5s)。同方程式预见的相反，自由旋转的甲基需要相当长的自旋晶格弛豫时间 (1.5s)。

43　T_1 (S)

(3) 分子片段柔动性　若由方程式 (3-9) 检查 2-甲醇 (42) 分子中各个^{13}C 的 T_1 值，会发现从 C-2 到 C-8 柔动性参数 nT_1 稳定增加。由于氢键的结果，分子靠近 OH 的部分是比较刚性的 (nT_1 在 3.5s 和 4.4s 之间)。离 OH 远的 C 柔动性增加，自旋晶格弛豫时间相应延长。2 个甲基的 nT_1 值也反映氢键的影响：离 OH 远者 nT_1 = 16.5s；近者 7.8s。

(4) 分子运动的各向异性　单取代苯环是很典型例子。如苯甲酸苯酯，取代基对位的 CH 比其邻位和间位者弛豫快，这是因为分子运动各向异性的结果，即苯环沿取代基和其对位的旋转轴旋转容易，导致取代基对位 C 原子的 T_1 比其邻间位者小。若苯环邻位被大体积的取代基占有，如2,2′,6,6′-四甲基联苯 (45)，则苯环对位 CHT_1 变大，即使苯环所有 CH 原子的 T_1 值难于区分。图 3-26 给出烟碱 (46) 分子中吡啶环的旋转各向异性，主轴系通过 C-3 和 C-6；C-6 比分子中其他 CH 弛豫地快。

44　　45　　46　T_1 (s)

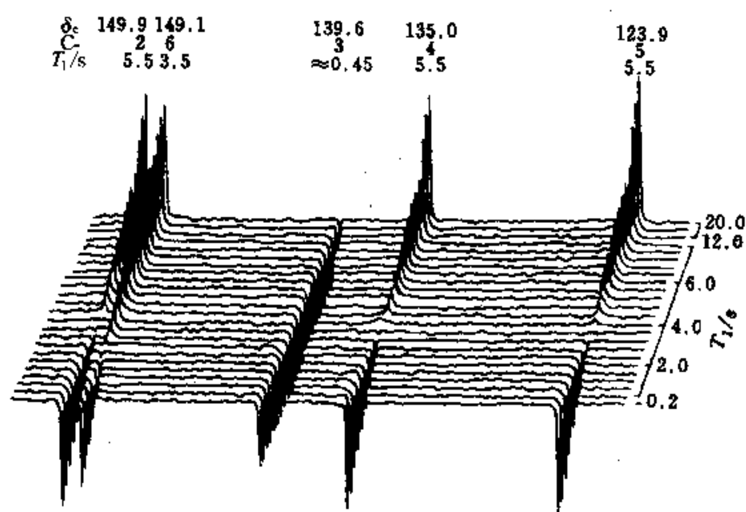
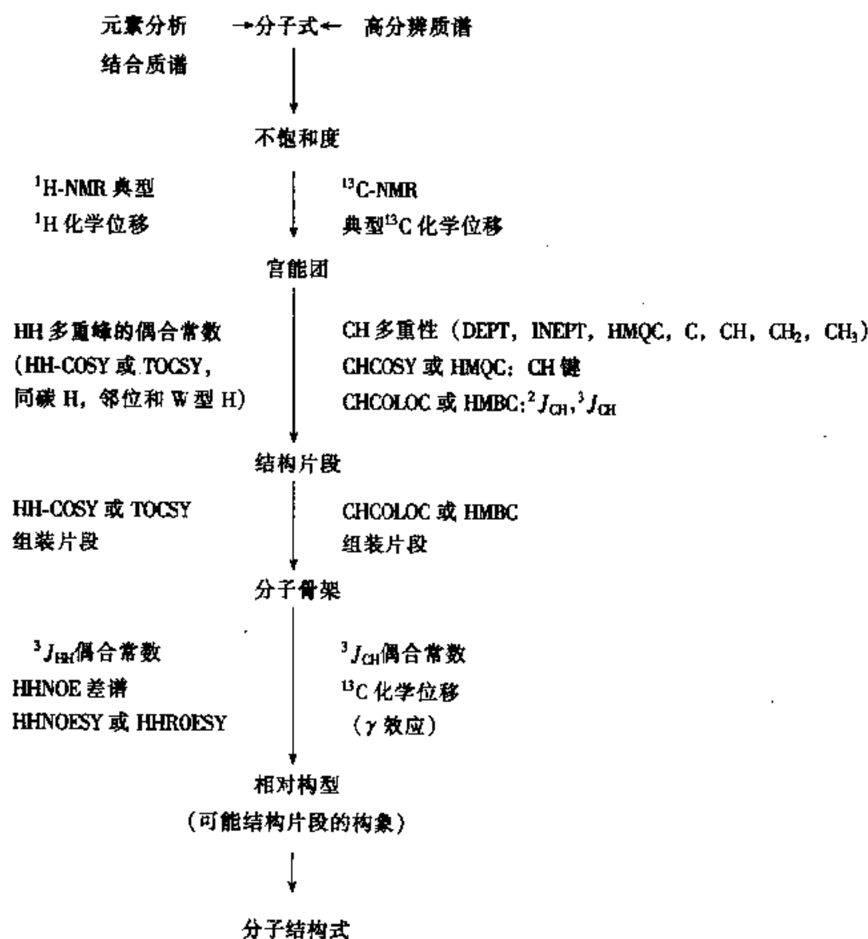


图 3-26 L-烟碱（46）吡啶环^{13}C核自旋晶格弛豫时测量序列
$[(CD_3)_2CO, \varphi = 75\%$，25℃，50MHz]

第七节 测定分子结构的程序综述

上述用 NMR 谱测定分子结构、构型和构象的方法，可概括为下列序程：



在进行有机分子的结构研究尤其是天然产物的结构研究中，常遇到两种情况：其一是分子的基本骨架已知，可能是分子中不同的功能基或不同的立体化学而成为未知的新化合物；其二是分子的骨架也是新的，即完全未知的化合物。属于第一种情况，结构研究较为容易，关键是先确定其结构类型，剩下的问题较易解决。第二种情况，对于完全未知的化合物，确定分子式是重要的，常用两种方法，高分辨质谱法和质谱加元素分析法。前者用量极微，微克量级便可。由分子式可算出分子的不饱和度，从而确定分子所含的不饱和键数和环的数目。有机化合物中常见的杂原子有 N、O、S 和 X 等，不饱和度的数目可根据以下方法由分子式求出：O 和 S 原子不取代 H 原子；X（卤素）原子取代一个 H，N 原子取代一个 CH，由此产生的实验式 C_nH_n，与饱和烷烃的实验式 $C_nH_{2n}+2$ 比较，得到缺少氢的数目 x，除 2，便求出不饱和度数，即$(2n+2-x)/2$。例如一个化合物分子式为 C_8H_9NO，根据上述计算方法得出实验式为 C_9H_{10}，与饱和烷烃的实验式相比缺少 10 个 H，所以该物含 5 个不饱和度。如果 NMR 谱在多重键化学位移范围不呈现信号，则不饱和度数便是该物所含环的数目。还有一个计算实验式的简便方法：分子式中的 nX 加 nH、nN 减 nH，O 和 S 不加不减，由此求出实验式。当然如果样品量和溶度允许，测 INADEQUATE 谱也是值得的。测定特定 C 的绝对构型可采用手性位移试剂法。构象和芳香性的信息可从各向异性和环电流效应获取。pH 效应可给出质子化位置。分子动力学的问题可由变温 NMR 和^{13}C 自旋晶格弛豫时间解决。

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第二篇　质子核磁共振谱的化学位移和偶合常数

第四章　一般有机化合物的质子核磁共振谱的化学位移和偶合常数

第一节　取代烃类化合物的^{1}H-NMR 化学位移

一、取代烷烃化合物的^{1}H-NMR 化学位移

表 4-1　单取代烷烃的^{1}H-NMR 化学位移数据[66]

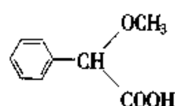
取代基	甲基	乙基		丙基			异丙基		叔丁基
	—CH_3	—CH_2	—CH_3	—CH_2	—CH_2	—CH_3	—CH	—CH_3	—CH_3
—H	0.23	0.86	0.86	0.91	1.33	0.91	1.33	0.91	0.89
—CH=CH_2	1.71	2.00	1.00						1.02
—C≡CH	1.80	2.16	1.15	2.10	1.50	0.97	2.59	1.15	1.22
—Ar	2.35	2.63	1.21	2.59	1.65	0.95	2.89	1.25	1.32
—F	4.27	4.36	1.24						1.34
—Cl	3.06	3.47	1.33	3.47	1.81	1.06	4.14	1.55	1.60
—Br	2.69	3.37	1.66	3.35	1.89	1.06	4.21	1.73	1.76
—I	2.16	3.16	1.88	3.16	1.88	1.03	4.24	1.89	1.95
—OH	3.39	3.59	1.18	3.49	1.53	0.93	3.94	1.16	1.22
—O—R	3.24	3.37	1.15	3.27	1.55	0.93	3.55	1.08	1.24
—OC=C	3.5	3.7	1.3						
—O—Ar	3.73	3.98	1.38	3.86	1.70	1.05	4.51	1.31	
—$OCOCH_3$	3.67	4.05	1.21	3.98	1.56	0.97	4.94	1.22	1.45
—OCO—Ar	3.88	4.37	1.38	4.25	1.76	1.07	5.22	1.37	1.58
—OSO_2—*p*-Ts	3.70	4.07	1.30	3.94	1.60	0.95	4.70	1.25	
—NH_2	2.47	2.74	1.10	2.61	1.43	0.93	3.07	1.03	1.15
—$NHCOCH_3$	2.71	3.21	1.12	3.18	1.55	0.96	4.01	1.13	1.28
—NO_2	4.29	4.37	1.58	4.28	2.01	1.03	4.44	1.53	1.59
—SH	2.00	2.44	1.31	2.46	1.57	1.02	3.16	1.34	1.43
—SR	2.09	2.49	1.25	2.43	1.59	0.98	2.93	1.25	1.39
—S—S—R	2.30	2.67	1.35	2.63	1.71	1.03			1.32
—CHO	2.20	2.46	1.13	2.42	1.67	0.97	2.39	1.13	1.07
—$COCH_3$	2.09	2.47	1.05	2.32	1.56	0.93	2.54	1.08	1.12
—CO—Ar	2.55	2.92	1.18	2.86	1.72	1.02	3.58	1.22	
—COOH	2.08	2.36	1.16	2.31	1.68	1.00	2.56	1.21	1.23
—$COOCH_3$	2.01	2.28	1.12	2.22	1.65	0.98	2.48	1.15	1.16
—$CONH_2$	2.02	2.23	1.13	2.19	1.68	0.99	2.44	1.18	1.22
—C=N—OH	1.9								
—CN	1.98	2.35	1.31	2.29	1.71	1.11	2.67	1.35	1.37

表 4-2　多取代烷烃的¹H-NMR 化学位移的计算[66]

$$\delta_{CH_2R_1R_2} = 1.25 + \sum_{1}^{2} a_i \qquad \delta_{CHR_1R_2R_3} = 1.50 + \sum_{1}^{3} a_i$$

取 代 基	a_i	取 代 基	a_i	取 代 基	a_i
—R	0.0	—OH	1.7	$—NO_2$	3.0
—C═C—	0.8	—O—R	1.5	—S—R	1.0
—C≡C—	0.9	—O—Ar	2.3	—CHO	1.2
—Ar	1.3	—OCO—R	2.7	—CO—R	1.2
—Cl	2.0	—OCO—Ar	2.9	—COOH	0.8
—Br	1.9	$—NH_2$	1.0	—COO—R	0.7
—I	1.4	$—N—R_2$	1.0	—CN	1.2

例如：



基值：　1.5
烷氧基：1.5
羧基：　0.8
苯基：　1.3

计算值：5.1
实验值：4.8

表 4-3　甲基的¹H-NMR 化学位移数据 (CH_3R)[40]

取 代 基	δ	取 代 基	δ	取 代 基	δ
$—CH_2CH_2R'$	0.88～1.05	$—OC(=O)R'$	3.67～3.87	$—C(=O)—CH(R')(R'')$	2.13～2.35
$—CH_2CH(R')(R'')$	0.90～1.13	$—CH_2SR'$	1.20～1.52	$—C(=O)—C(R')=C(R'')(R'')$	1.88～2.68
$—CH_2C(R')(R'')(R''')$	0.83～1.24	$—CH_2Ph$	1.25～1.30	$—C(Ph)=C(R'')—C(R''')(R')$	2.12～2.40
$—CH_2XX$	1.48～1.83	$—CH(CH_3)—CH_2R$	0.82～0.93	$—N(R')(R'')$	2.25～2.57
$—CH_2C(=O)—R'$	1.05～1.23	$—CH(CH_3)—CH(R')(R'')$	0.82～1.02	$—N(R'')—C(=O)—R'$	2.83～3.07
$—CH_2—C(R')(R'')$	0.97～1.23	$—CH(CH_3)—C(R')(R'')(R''')$	0.75～0.97	$—N(Ph)(R')$	2.87～3.05
$—CH_2—N(R')(R'')$	0.97～1.13	$—CH(CH_3)—C(=O)—R'$	1.10～1.22	$—N(C(=O)R')(Ph)$	3.20～(4.00)
$—CH_2OR'$	1.20～1.47	$—C(CH_3)_2—CH_2R'$	0.72～1.02	—Ph	1.53～2.78
$—CH_2OC(=O)R'$	1.25～1.40	$—C(CH_3)_2—Ph$	1.30～1.43	—Ar	-4.23～2.97
$—CH(CH_3)—Ph$	1.22～1.25	$—C(=O)—CH_2—R'$	2.12～2.17		
$—C(R')(R'')H$	0.90～0.95				
$—N(Ph)(C═)$	3.02～(3.90)				
—O—R'	3.33～3.47				
—O—Ar	3.67～4.40				

续表

取代基	δ	取代基	δ	取代基	δ
—C(H)=R′	0.82～1.29	—C(CH₃)=R′	0.67～1.27	—C(H)=C(R″)—C(R‴)=R′	1.60～2.11
—C(CH₂R′)(X)R″	1.58～1.92	—CH(CH₂R′)OR″	1.12～1.44		
—CH(CH₂R′)—N(R″)(R″)(R‴)	1.05～1.69	—C(=O)—N(R′)(R″)(R‴)	1.87～2.50	—C(C(=O)R′)=C(R″)—C(R‴)=R‴′	1.61～2.27
		—C(=O)—Ph	2.47～2.59		
R″R‴N—C(CH₂R′)(CH₃)—	1.12～1.75	—C(=O)—OR′	1.92～2.25		
		—C(=O)OPh	2.06～(2.58)		
—OC(=O)—C(=R″)R′	3.62～3.96	—C(CH₃)=C(R″)—C(R‴)=R′	1.60～2.18	—C(N<(或 O))=C(R″)—C(R‴)=R′	1.92～2.40
—S—R′	2.08～2.12				

表 4-4 烷烃 β-取代基效应[1]

以 δ = 0.9(CH_3—),1.25(—CH_2—)及 1.5(CH)为计算标准。如，CH_3—C—C═C ，则 $\delta_{CH_3} = 0.9 + 0.1 = 1.0$。

X	CH_3—C—X	CH_2—C—X	CH—C—X
—C—C	+0.1	±0.05	
—CO·OH ， —CO·OR	+0.25	—	
—CN		+0.4	
—CO·NH_2	+0.23		
—CO·R ， —CHO	+0.2	—	
—SH,—SR	+0.45	+0.3	
—NH_2,—NR_2	+0.1	+0.05	
—I	+1.0	+0.5	+0.4
—Ph	+0.35	+0.3	
—Br	+0.8	+0.6	+0.25
—NH·CO·R	+0.1		
—Cl	+0.6	+0.4	+0.02
—OH,—OR	+0.27	+0.1	
—O·CO·R	+0.37		
—O·Ph	—	+0.35	
—F	—	+0.2	
—NO_2	+0.67	+0.8	

表 4-5　二取代亚甲基的¹H-NMR 化学位移计算

$$\delta_{CH_2R_1R_2} = 0.23 + Z_R^1 + Z_R^2$$

R	Z_R	R	Z_R	R	Z_R
$-C_nH_{2n+1}$	0	$-OCOph$	3.23	$-SH$	1.63
$-C=C-$	1.33	$-NH_2$	1.69	$-SC_nH_{2n+1}$	1.63
$-C\equiv CH$	1.52	$-NHC_nH_{2n+1}$	1.60	$-Sph$	1.92
$-C\equiv C_nH_{2n-1}$	1.52	$-N(C_nH_{2n+1})_2$	1.41	$-COC_nH_{2n+1}$	1.58
$-C\equiv CC_6H_5$	1.77	$-NHph$	2.15	$-COph$	2.08
$-C_6H_5$	1.85	$-N(C_nH_{2n+1})ph$	2.39	$-COOH$	1.49
$-F$	3.15	$-NH_3^+$	2.31	$-COOC_nH_{2n+1}$	1.49
$-Cl$	2.48	$-NH_2^+C_nH_{2n+1}$	2.31	$-COOph$	1.74
$-Br$	2.29	$-NH^+(C_nH_{2n+1})_2$	2.46	$-CONH_2$	1.39
$-OH$	2.46	$-N^+(C_nH_{2n+1})_3$	2.56	$-CON(C_nH_{2n+1})_2$	1.39
$-OC_nH_{2n+1}$	2.27	$-NHCOC_nH_{2n+1}$	2.23	$-CONHph$	1.59
$-Oph$	2.89	$-N(C_nH_{2n+1})COC_nH_{2n+1}$	2.23	$-C\equiv N$	1.73
$-OCOC_nH_{2n+1}$	2.98	$-NHCOph$	2.33		

表 4-6　带有不同取代基的二取代亚甲基¹H-NMR 化学位移计算

$$\delta_{R^1CH_2-CR^2R^3R^4} = 1.20 + Z_R^1 + Z_R^2 + Z_R^3 + Z_R^4$$

R	Z_R(α-效应)	$Z_{R'}$①(β-效应)	R	Z_R(α-效应)	$Z_{R'}$①(β-效应)
$-C_nH_{2n+1}$	0.00	0.00	$-NH_3^+$;$-NH_2^+C_nH_{2n+1}$	1.77	0.60
$-C=C-$	0.78	0.16	$-NH^+(C_nH_{2n+1})_2$	1.95	0.60
$-C\equiv CH$;$-C\equiv C_nH_{2n+1}$	0.98	0.21	$-N^+(C_nH_{2n+1})_3$	2.07	0.70
$-C\equiv Cph$	1.23	0.21	$-NHCOC_nH_{2n+1}$;	1.79	0.26
$-ph$	1.31	0.37	$-N(C_nH_{2n+1})COC_nH_{2n+1}$		
$-F$	2.76	0.24	$-NHCOph$	1.89	0.26
$-Cl$	2.04	0.36	$-SH$;$-SC_nH_{2n+1}$	1.15	0.30
$-Br$	1.87	0.52	$-Sph$	1.44	0.28
$-OH$	2.07	0.23	$-COC_nH_{2n+1}$	1.11	0.38
$-OC_nH_{2n+1}$	1.91	0.28	$-COph$	1.61	0.58
$-Oph$	2.48	0.58	$-COOH$;	1.02	0.34
$-OCOC_nH_{2n+1}$	2.61	0.43	$-COOC_nH_{2n+1}$		
$-OCOph$	2.91	0.53	$-COOph$	1.27	0.34
$-NH_2$	1.27	0.25	$-CONH_2$;	0.89	0.40
$-NHC_nH_{2n+1}$	1.23	0.25	$-CON(C_nH_{2n+1})_2$		
$-N(C_nH_{2n+1})_2$	1.00	0.25	$-CONHph$	1.09	0.40
$-NHph$	1.74	0.31	$-C\equiv N$	1.15	0.42
$-N(C_nH_{2n+1})ph$	1.97	0.31			

① R′代表 R^2、R^3、R^4 的总称。

表 4-7　卤代甲烷及卤代乙烷的¹H-NMR 化学位移数据[66]

化合物类型 \ X	F	Cl	Br	I	化合物类型 \ X	F	Cl	Br	I
CH_3X	4.27	3.06	2.69	2.16					
CH_2X_2	5.45	5.33	4.94	3.90	CHX_2		5.8	5.86	
CHX_3	6.49	7.24	6.82	4.91	CH_3		2.1	2.47	
CH_2-X	4.36	3.47	3.37	3.16					
CH_3	1.24	1.33	1.66	1.88	XCH_2CH_2X		3.7	3.63	3.7

表 4-8 醇类甲基的¹H-NMR 化学位移数据[2]

醇	甲基①	CH_3 和 $R_2CH—OH$ 间 C—C 键数目	δ 醇	δ 3,5-二硝基苯甲酸酯	醇	甲基①	CH_3 和 $R_2CH—OH$ 间 C—C 键数目	δ 醇	δ 3,5-二硝基苯甲酸酯
2-辛醇	α	1	1.11	1.42	3-辛醇	ω	5	0.90	0.90
2-癸醇	α	1	1.11	1.43	5-癸醇	ω	5	0.91	0.90
2-十二烷醇	α	1	1.12	1.43	6-十二烷醇	α	5	0.89	0.90
3-辛醇	α	2	0.91	1.00	4-辛醇	ω	6	0.89	0.89
3-癸醇	α	2	0.91	1.00	6-十二烷醇	ω	6	0.89	0.88
3-十二烷醇	α	2	0.91	1.00	3-辛醇	ω	7	0.88	0.87
4-辛醇	α	3	0.92	0.98	5-十二烷醇	ω	7	0.89	0.87
4-癸醇	α	3	0.93	0.98	4-十二烷醇	ω	8	0.89	0.87
4-十二烷醇	α	3	0.92	0.98	3-十二烷醇	ω	9	0.88	0.87
4-辛醇	ω	4	0.92	0.93	2-辛醇	ω	6	0.89	0.89
5-癸醇	α	4	0.93	0.93	2-癸醇	ω	8	0.89	0.88
5-十二烷醇	α	4	0.93	0.93	2-十二烷醇	ω	10	0.89	0.87

① α 表示 C_1 位；ω 表示另一端甲基。

表 4-9 不饱和酮烷基的¹H-NMR 化学位移数据[3]

化合物	δ β-CH_3 顺	δ β-CH_3 反	δ β-CH_2 顺	δ β-CH_2 反	化合物	δ β-CH_3 顺	δ β-CH_3 反	δ β-CH_2 顺	δ β-CH_2 反
$C(CH_3)_2=CHCOCH_3$	2.11	1.83	—	—	$CCH_3Pr=CEtCOCH_3$	1.70	—	—	2.14
$C(CH_3)_2=CHCOEt$	2.09	1.85	—	—	$C(CH_3)_2=CCH_3COEt$	1.74	1.74	—	—
$CEtCH_3=CHCOEt$	—	1.85	2.54	—	$CEt_2=CCH_3COEt$	—	—	2.10	2.08
$CCH_3Et=CHCOEt$	2.11	—	—	2.14	$CEt_2=CCH_3COi\text{-}Pr$	—	—	2.04	1.95
$C(CH_3)_2=CHCOPr$	2.05	1.82	—	—	$C(CH_3)_2=CCH_3COCH_3$	1.82	1.72	—	—
$CCH_3Pr=CHCOCH_3$	2.05	—	—	2.05	$CEtCH_3=CCH_3COCH_3$	—	1.72	2.25	—
$CCH_3Pr=CHCOPr$	2.07	—	—	2.08	$CCH_3Et=CCH_3COCH_3$	1.81	—	—	2.11
$CPrCH_3=CHCOPr$	—	1.84	2.54	—	$CHEt=CCH_3COEt$	—	—	2.24	—
$C(CH_3)_2=CEtCOCH_3$	1.74	1.74	—	—	$CHCH_3=CCH_3COCH_3$	—	1.72	—	—
$CPrCH_3=CEtCOCH_3$	—	1.70	2.14	—					

表 4-10 叔丁基的¹H-NMR 化学位移数据[4]

化合物	δ_{CMe_3}	化合物	δ_{CMe_3}
叔丁基环己烷	0.85	Me_3COCMe_3	1.24
$Me_3C—CH_2CHMe_2$	0.86	$Me_3C—SC_6H_5$	1.26
$Me_3C—CMe_3$	0.87	$p\text{-}Me_3C—C_6H_4OH$	1.27
$Me_3C—H$	0.90	$Me_3C—SCH_3$	1.27
$Me_3C—CH_3$	0.92	$Me_3C—SS—CMe_3$	1.28
4-叔丁基环己酮	0.92	$p\text{-}Me_3C—C_6H_4OCH_3$	1.28
$Me_3C—CH=CH_2$	1.00	$3,5\text{-}(Me_3C—)_2C_6H_3OH$	1.28
$Me_3C—NH_2$	1.10	$3\text{-}Me_3C\text{-}5\text{-}CH_3C_6H_5CH_3$	1.28
$Me_3C—OC_2H_5$	1.13	$p\text{-}Me_3C—C_6H_4CH_3$	1.28
$Me_3C—OCH_3$	1.13	$p\text{-}Me_3C—C_6H_4SH$	1.28
$Me_3C—CONH_2$	1.16	$m\text{-}Me_3C—C_6H_4OH$	1.28
$Me_3C—O_2—CMe_3$	1.17	$1,2,4\text{-}(Me_3C—)_3C_6H_3$	1.29
$Me_3C—O_2H$	1.19	$p\text{-}Me_3C—C_6H_4CH_2CH_3$	1.29
$Me_3C—C\equiv CH$	1.20	$Me_3C—NH_2BH_3$	1.30
$Me_3C—OH$	1.20	$p\text{-}Me_3C—C_6H_4Br$	1.30
$Me_3C—CO_2H$	1.22	$m\text{-}(Me_3C)_2—C_6H_4$	1.31

续表

化合物	δ_{CMe_3}	化合物	δ_{CMe_3}
p-$(Me_3C)_2C_6H_4$	1.31	$Me_3C—SH$	1.41
$Me_3C—C_6H_5$	1.32	$(Me_3C—)_2SO_2$	1.44
叔丁基吡啶	1.32	$Me_3C—NC$	1.44
Me_3CF	1.33	5-Me_3C-2,4,6-$(NO_2)_3C_6Me_2$	1.46
1,3,5-$(Me_3C)_3C_6H_3$	1.34	$Me_3C—O_2CCH=CH_2$	1.45
p-$Me_3C—C_6H_4—CO_2CH_3$	1.34	1,2,4,5-$(Me_3C)_4C_6H_2$	1.48
$Me_3C—NHCHO$	1.35	1,2,4-$(Me_3C)_3—C_6H_3$	1.52
p-$Me_3C—C_6H_4CO_2CH_3$	1.35	1,2,4-$(Me_3C)_3—C_6H_3$	1.43
m-$Me_3C—C_6H_4CO_2CH_3$	1.36	O—$(Me_3C)_2—C_6H_4$	1.54
p-$Me_3C—C_6H_4NO_2$	1.36	$Me_3C—NO_2$	1.59
$(Me_3C—)_2S$	1.39	$Me_3C—Cl$	1.59
$Me_3C—O_2CCH_3$	1.40	$Me_3C—Br$	1.77
2,6-$(Me_3C—)$-4-$CH_3C_6H_2OH$	1.40	$Me_3C—I$	1.94

表 4-11　乙基金属化合物的^{1}H-NMR 化学位移数据[5]

金属	族	δ_{CH_3}	δ_{CH_2}	金属	族	δ_{CH_3}	δ_{CH_2}
Li	Ⅰ	1.0～2.0	−0.5～−1.0	Si,Ge,Sn,Pb	Ⅳ	1.0～2.0	0.0～2.0
Mg	Ⅱ	1.0～2.0	−0.5～−1.0	Se,Te	Ⅵ	1.0～2.0	2.0～3.0
Al,Ga,Tl	Ⅲ	0.5～2.0	−0.5～2.7	Zn,Cd,Hg		1.0～2.0	0.5～2.5

表 4-12　甲基金属化合物的^{1}H-NMR 化学位移数据[5]

金属	族	δ_{CH_3}	金属	族	δ_{CH_3}	金属	族	δ_{CH_3}
Li	Ⅰ	−1.3～−1.5	Si,Ge,Sn,Pb	Ⅳ	0.0～1.0	Zn,Cd		−1.0～0.0
Be,Mg	Ⅱ	−1.0～−1.5	As,Sb,Bi	Ⅴ	0.3～0.6	Hg		0.0～1.0
Al,Ga,In,Tl	Ⅲ	−0.5～0.6	Se,Te	Ⅵ	2.0	Pt,Rh,Ir		0.0～1.5

二、芳环取代烷基化合物的^{1}H-NMR 化学位移

表 4-13　芳香甲基的^{1}H-NMR 化学位移数据[6]

化合物	结构式	甲基位置	δ_{CH_3}	化合物	结构式	甲基位置	δ_{CH_3}
苯		1 1,2 1,3 1,4 1,3,5 1,2,4,5 1,2,3,4,5 1,2,3,4,5,6	2.37 2.25 2.30 2.28 2.25 2.15 2.13,2.18 2.17	菲		1 2 3 9	2.73 2.53 2.62 2.72
				蒽		2 9 9,10	2.55 3.05 3.05
萘		1 2 1,2 1,5 1,6 2,3 2,3,6	2.68 2.50 2.47,2.57 2.70 2.50,2.63 2.40 2.38,2.47	芘		1 2 4	2.93 2.80 2.87
				薁		1	3.30

表 4-14　甲苯衍生物的^{1}H-NMR 化学位移数据[7]

取代基	δ_{CH_3}			取代基	δ_{CH_3}		
	邻位	间位	对位		邻位	间位	对位
Cl	2.36	2.32	2.30	CN	2.51	2.42	2.42
Br	2.40	2.33	2.26	NO_2	2.45	2.47	2.58
I	2.39	2.29	2.29	OCH_3	2.18	2.30	2.27

表 4-15 芳香取代烷的¹H-NMR 化学位移[66]

17

甲基位置	δ_{CH_3}
2	2.55
3	2.32
4	2.37

18

甲基位置	δ_{CH_3}
1	3.60
2	3.20
3	2.30

第二节 含氧化合物的¹H-NMR 化学位移和偶合常数

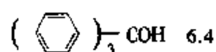
一、醇和醚类化合物的¹H-NMR 化学位移和偶合常数

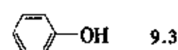
(一) 脂肪醇羟基氢的化学位移[66]

(以二甲基亚砜为溶剂)

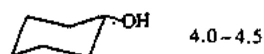

CH₃CH₂OH 4.5

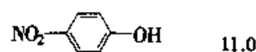

CCl₃CH₂OH 6.8

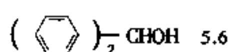

(C₆H₅)₃COH 6.4

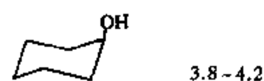

C₆H₅OH 9.3

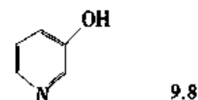

C₆H₅CH₂OH 5.2


4.0~4.5


NO₂-C₆H₄-OH 11.0


(C₆H₅)₂CHOH 5.6


3.8~4.2

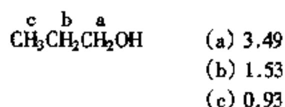

9.8

(二) 脂肪醇烷基氢的化学位移


CH₃OH (a) 3.39


(CH₃)₂CHOH (a) 3.94 (b) 1.16


CH₃CH₂OH (a) 3.59 (b) 1.18


CH₃CH₂CH₂OH (a) 3.49 (b) 1.53 (c) 0.93

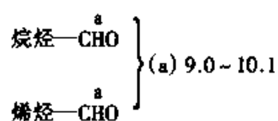

(CH₃)₃COH (a) 1.22

(三) 脂肪醚的¹H-NMR 化学位移和偶合常数

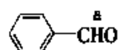
化合物	化学位移	化合物	化学位移
$\overset{a}{CH_3}O—R$	(a) 3.24	$\overset{b}{CH_3}\overset{a}{CH_2}OR$	(a) 3.37 (b) 1.15
$\overset{a}{CH_3}O—C=C$	(a) 3.5	$\overset{b}{CH_3}\overset{a}{CH_2}O—C=C$	(a) 3.7 (b) 1.3
$\overset{a}{CH_3}O$—C₆H₅ (H$_b$ 邻位)	(a) 3.73 $\lvert J\rvert_{ab}=0\sim0.8$	$\overset{b}{CH_3}\overset{a}{CH_2}O$—C₆H₅	(a) 3.98 (b) 1.38
$CH_3O\overset{a}{CH_3}$	(a) 3.3	$\overset{b}{CH_2}(O\overset{a}{CH_3})_2$	(a) 3.3 (b) 4.5
$\overset{b}{CH}(O\overset{a}{CH_3})_3$	(a) 3.3 (b) 5.1	$(\overset{b}{CH_3})_2\overset{a}{CH}OR$	(a) 3.55 (b) 1.08

二、醛酮类化合物的¹H-NMR 化学位移和偶合常数

(一) 脂肪醛类化合物的¹H-NMR 化学位移和偶合常数[66]

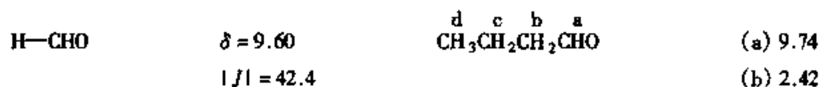


烷烃—$\overset{a}{CHO}$
烯烃—$\overset{a}{CHO}$
(a) 9.0～10.1



无邻位取代 (a) 9.6～10.2

含邻位取代 (a) 10.2～10.5

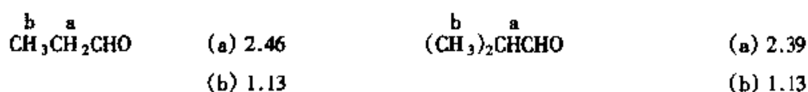


H—CHO $\delta=9.60$, $\lvert J\rvert=42.4$

$\overset{d}{CH_3}\overset{c}{CH_2}\overset{b}{CH_2}\overset{a}{CHO}$ (a) 9.74 (b) 2.42 (c) 1.67 (d) 0.97 $J_{ab}=2$



$\overset{b}{CH_3}\overset{a}{CHO}$ (a) 9.80 (b) 2.20 $J_{ab}=3$



$\overset{b}{CH_3}\overset{a}{CH_2}CHO$ (a) 2.46 (b) 1.13

$(\overset{b}{CH_3})_2\overset{a}{CH}CHO$ (a) 2.39 (b) 1.13



$(\overset{a}{CH_3})_3CCHO$ (a) 1.07



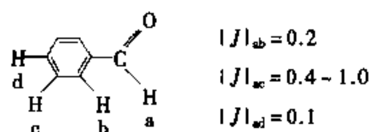
$\lvert J\rvert_{HC—CHO}=0-3$



$\lvert J\rvert_{ab}=8$

$\lvert J\rvert_{ac}=0.3$

$\lvert J\rvert_{ad}=0.1$



$\lvert J\rvert_{ab}=0.2$

$\lvert J\rvert_{ac}=0.4\sim1.0$

$\lvert J\rvert_{ad}=0.1$

(二) 脂肪酮类化合物的^{1}H-NMR 化学位移和偶合常数[66]

$\overset{a}{CH_3}COCH_3$ (a) 2.09

$\overset{a}{CH_3}COC{-}C$ (a) 2.3

$\overset{b}{CH_3}\overset{a}{CH_2}COCH_3$ (a) 2.47 (b) 1.05

$\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CH_2}COCH_3$ (a) 2.32 (b) 1.56 (c) 0.93

$(\overset{b}{CH_3})_2\overset{a}{CH}COCH_3$ (a) 2.54 (b) 1.08

$(\overset{a}{CH_3})_3CCOCH_3$ (a) 1.12

$\overset{a}{CH_3}CO\overset{b}{CH_2}COCH_3$ (a) 2.17 (b) 3.62

$\overset{a}{CH_3}CO-C_6H_5$ (a) 2.55

$\overset{b}{CH_3}\overset{a}{CH_2}CO-C_6H_5$ (a) 2.92 (b) 1.18

$\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CH_2}CO-C_6H_5$ (a) 2.86 (b) 1.72 (c) 1.02

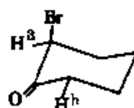
$(\overset{b}{CH_3})_2\overset{a}{CH}CO-C_6H_5$ (a) 3.58 (b) 1.22

H–C–C(=O)–C–H

$J_{HCCOCCH} = 0 \sim 0.5$

5,5-二甲基-3-(NH-CH$_2$-R)环己-2-烯酮（CH$_3$，CH$_3$；O；α；NH γ；CH$_2$ β）

R	δ_{CH_3}	δ_α	δ_β	δ_γ	$\delta_{环CH_2}$
C_6H_5	1.04	5.08	4.20	5.9	2.10，2.23
CF_3	1.08	5.23	3.71		2.19，2.26



(三) 环酮类化合物的^{1}H-NMR 化学位移和偶合常数[66]

环丙酮：(a) 1.65

环丁酮：(a,c) 3.03 (b) 1.96 $J_{ac(cis)} = 1.9$ $J_{ac(trans)} = 1.0$

环戊酮：(a) 2.06 (b) 2.02

环己酮：(a) 2.22 (b,c) ≈ 1.8

环丁-1,2-二酮：(a) 3.0

环己-1,3-二酮：(a) 3.4

1-茚酮：(a) 2.60 (b) 3.08

2-茚酮：(a) 3.50

1,3-茚二酮：(a) 3.23

1-四氢萘酮：(a) 2.58 (b) 2.18 (c) 2.92 (d,e,f) 7.0 ~ 7.4 (g) 8.0

对苯醌：(a) 6.78

三、环醚化合物的^{1}H-NMR 化学位移和偶合常数[66]

(a) 2.54

$J_{gem}=6$
$J_{cis}=4.5$
$J_{trans}=3.1$

(a,c) 4.73
(b) 2.72

(a) $J_{gem}=-5.8$
(b) $J_{gem}=-11.0$
$J_{cis}=8.7$
$J_{trans}=6.6$
$|J|_{ac}<0.3$Hz

(a) 3.75
(b) 1.85

(a) 4.20
(b) 2.53
(c) 4.82
(d) 6.22

$J_{ab}=9.3$
$J_{bc}=2.5$
$J_{bd}=2.6$
$J_{cd}=2.6$

(a,d) 4.43
(b,c) 5.78

$J_{ab}\approx 1$
$J_{ac}\approx -1$
$J_{bc}\approx 6$

(a) 3.9
(b) 4.9

(a) $J_{gem}=-7.5$
$J_{cis}=7.3$
$J_{trans}=6.0$

(a) 5.90

(a) $|J|_{gem}=1.5$

(a) 3.6
(b,c) 1.6

(a) 4.0
(b) ≈1.9
(c) ≈1.9
(d) 4.6
(e) 6.4

(a,e) 6.17
(b,d) 4.63
(c) 2.66

$J_{ab}=7.0$
$J_{ac}=1.7$
$J_{ae}=1.5$
$J_{bc}=3.4$

(a,d) 6.35
(b,c) 7.71

$J_{ab}=5.9$　$J_{ac}=0.4$
$J_{ad}=2.7$　$J_{bc}=1.1$

(a) 3.71

(a) 4.70
(b) 3.80
(c) 1.68

(a) 5.00

(a) 3.67
(b) 2.87
(c) 1.92

(a) 3.88
(b) 2.57

取代基	位置	δ_2	δ_{4e}	δ_{4a}	δ_{5e}	δ_{5a}
t-Bu	2	3.95			1.20	1.91
$C_6H_4OCH_3(p)$	2	5.20			1.19	1.97
$C_6H_4OCH_3(m)$	2	5.70			1.20	2.03
胡椒基	2	5.18			1.19	1.98
t-Bu	5		3.97	3.40	(1.64)	

$\delta_{CH_3}=1.16, 0.74$　$\delta_{4e}=3.62$　$\delta_{4a}=3.45$
$\delta_{2e}=5.04$　$\delta_{2a}=4.56$

R	δ_2	J_{4e5a}	J_{4a5a}
Me	4.40	5.6	10.6
Et	4.20	4.4	11.2
i-Pr	4.03	4.5	11.3
t-Bu	3.86	4.7	12.1

四、含羰基化合物的¹H-NMR化学位移和偶合常数

（一）脂肪羧酸化合物的¹H-NMR化学位移[66]

R—COOH (a), C_6H_5—COOH (a)　(a) 10～13

化合物	化学位移	化合物	化学位移
CH_3COOH	(a) 2.08	$(CH_3)_2CHCOOH$	(a) 2.56 (b) 1.21
CH_3CH_2COOH	(a) 2.36 (b) 1.16	$(CH_3)_3CCOOH$	(a) 1.23
$CH_3CH_2CH_2COOH$	(a) 2.31 (b) 1.68 (c) 1.00		
$HOOCH_2COOH$	(a) 3.4		
$HOOCCH_2CH_2COOH$	(a) 2.6		

（二）脂肪酯化合物的¹H-NMR化学位移和偶合常数[66]

化合物	δ	化合物	δ / J
$\overset{a}{H}COOCH_3$	(a) 8.03	$\overset{a}{H}COOC(H_b)-C(H_c)-$	$J_{ab}\approx-1$; $J_{ac}\approx0.5$
$\overset{a}{H}COO(H_b)C=C(H_c)(H_d)$	(a) 8.1	$J_{ab}=-0.7$; $J_{ac}=1.6$; $J_{ad}=0.8$	ROCO-C₆H₃(OH)（3-羟基苯甲酸酯）: 7.37, 8.04, 7.44, 7.75
$\overset{a}{CH_3}CO\overset{b}{OCH_3}$	(a) 2.01	(b) 3.67	
$\overset{a}{CH_3}COOC=C$	(a) 2.1		ROCO-C₆H₄-OH（2-羟基苯甲酸酯）: 7.83, 6.92, 7.37, 6.92
$\overset{a}{CH_3}COO-C_6H_5$	(a) 2.1		
$\overset{b}{CH_3}\overset{a}{CH_2}COOCH_3$	(a) 2.28	(b) 1.12	ROCO-C₆H₄-OCH₃（2-甲氧基苯甲酸酯）: 8.10, 7.10, 7.60, 7.10
$(\overset{b}{CH_3})_2\overset{a}{CH}COOCH_3$	(a) 2.48	(b) 1.15	
$\overset{a}{CH_3}OCOCH_3$	(a) 3.67	$\overset{a}{CH_3}OCO-C_6H_5$	(a) 3.88
$\overset{a}{CH_3}OCOC=C$	(a) 3.8	$\overset{a}{CH_3}OSO_2-C_6H_4-CH_3$	(a) 3.70
$\overset{b}{CH_3}\overset{a}{CH_2}OCOCH_3$	(a) 4.05 (b) 1.21	$\overset{b}{CH_3}\overset{a}{CH_2}OCO-C_6H_5$	(a) 4.37 (b) 1.38
$CH_3\overset{a}{CH_2}OCOCF_3$	(a) 4.3	$\overset{b}{CH_3}\overset{a}{CH_2}OSO_2-C_6H_4-CH_3$	(a) 4.07 (b) 1.30
$\overset{b}{CH_3}\overset{a}{CH_2}OCOC\equiv C$	(a) 4.3 (b) 1.3	$\overset{b}{CH_3}\overset{a}{CH_2}ONO$	(a) 4.78 (b) 1.39
$(\overset{b}{CH_3})_2\overset{a}{CH}OCOCH_3$	(a) 4.94 (b) 1.22		
$(\overset{b}{CH_3})_2\overset{a}{CH}OCO-C_6H_5$	(a) 5.22 (b) 1.37	$(\overset{b}{CH_3})_2\overset{a}{CH}OSO_2-C_6H_4-CH_3$	(a) 4.70 (b) 1.25

（三）内酯化合物的¹H-NMR化学位移和偶合常数[66]

化合物	δ	J	化合物	δ
β-丙内酯（a, b）	(a) 4.29 (b) 3.56		γ-丁内酯（a, b, c）	(a) 4.3 (b) 2.1 (c) 2.3
2(5H)-呋喃酮（a, b, c）	(a) 4.92 (b) 7.63 (c) 6.15		δ-戊内酯（a, b, c, d）	(a) 4.09 (b), (c) ≈1.6 (d) 3.31
2-吡喃酮（a, b, c, d）	(a) 7.77 (b) 6.43 (c) 7.56 (d) 6.38	$J_{ab}=5.0$ $J_{bc}=6.3$ $J_{cd}=9.4$		$J_{ac}=2.4$ $J_{bd}=1.5$ $J_{ad}=1.3$

（四）酰胺的¹H-NMR化学位移和偶合常数[66]

R—CONH₂ (a)；C₆H₅—CONH₂ (a)　} (a) 5～7

R—CONH(a)—R；C₆H₅—CONH(a)—R　} (a) 6～8.5

R—CONH(a)—C₆H₅；C₆H₅—CONH(a)—C₆H₅　} (a) 7.5～9.5

H(a)(C=O)—N(H(b))(CH₃(c))

Ⅰ(≈90%)

Ⅰ:(a) 8.1
(b) 7.9
(c) 2.74

H(a)(C=O)—N(CH₃(c))(H(b))

Ⅱ(≈10%)

Ⅱ:(a) 8.1
(b) 7.9
(c) 2.88

H(a)—CONH(b)—C₆H₅　(a) 8.2～8.7
(b) 7.5～9.5

H(a)(C=O)—N(CH₃(b))(CH₃(c))　(a) 8.02　$|J|_{ab}$≈0.3
(b) 2.97　$|J|_{ac}$≈0.7
(c) 2.88

H(C=O)—N(CH(b)(CH₃(c))₂)(CH₃(a))　⇌　H(C=O)—N(CH₃(a))(CH(b)(CH₃(c))₂)

Ⅰ(≈70%)

Ⅰ:(a) 2.71
(b) 4.12
(c) 1.19

Ⅱ(≈30%)

Ⅱ:(a) 2.83
(b) 4.78
(c) 1.10

CH₃(a)NH(b)COCH₃(c)　(a) 2.71
(b) 8.1
(c) ≈2.0

CH₃(a)CH₂(b)NH(c)COCH₃(d)　(a) 1.12
(b) 3.21
(c) 8.2
(d) ≈2.0

(CH₃)₂(a)CH(b)NH(c)COCH₃(d)　(a) 1.13
(b) 4.01
(c) 8.1
(d) ≈2.0

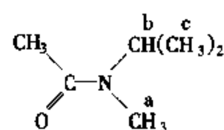
(CH₃)₃(a)CNH(b)COCH₃(c)　(a) 1.28
(b) 7.3
(c) ≈2.0

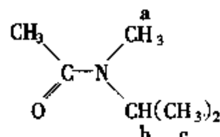
CH₃(a)CONH—C₆H₅　(a) ≈2.1

R—CO—N(哌啶，a、b为N旁CH₂)　(a,b) 3.36

CH₃(a)(C=O)—N(CH₃(b))(CH₃(c))　(a) 2.08
(b) 2.94
(c) 3.02

CH₃(a)CO—N(吡咯烷，b、e为N旁CH₂，c、d为环上CH₂)　(a) 2.05
(b,e) 3.46
(c,d) 1.97



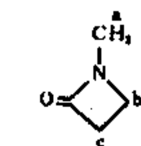


Ⅰ(≈40%)

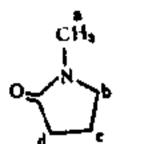
Ⅰ:(a) 2.70
(b) 3.92
(c) 1.15

Ⅱ(60%)

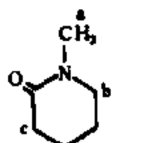
Ⅱ:(a) 2.83
(b) 4.52
(c) 1.03



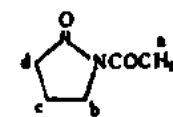
(a) 2.75
(b) 3.20
(c) 2.82



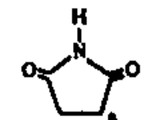
(a) 2.83
(b) 3.40
(c) ≈2.0
(d) 2.23



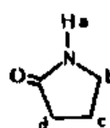
(a) 2.88
(b) 3.32
(c) 2.27



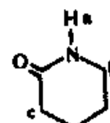
(a) 2.50
(b) 3.83
(c) 2.06
(d) 2.62



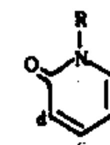
(a) 2.73



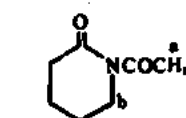
(a) 7.67
(b) 3.40
(c) ≈2.1
(d) 2.23



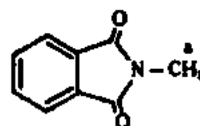
(a) 8.13
(b) 3.17
(c) 2.3



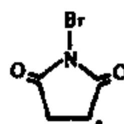
(a) 7.3
(b) 6.2
(c) 7.3
(d) 6.6



(a) 2.36
(b) 3.48

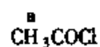


(a) 3.16



(a) 2.97

(五) 酰卤和酸酐等化合物的^{1}H-NMR 化学位移和偶合常数[66]



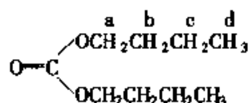
(a) 2.8



(a) 2.7

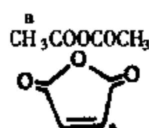


(a) 3.01

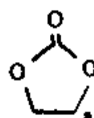


(a) 4.13
(b,c) 1.2～1.7
(d) 0.93

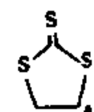
$\overset{a}{CH_3}COOCOCH_3$ (a) 2.2



(a) 7.1



(a) 4.20



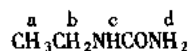
(a) 3.94



(a) 2.7
(b) ≈6

$\overset{a}{CH_3}\overset{b}{CH_2}NHCONHCH_2CH_3$

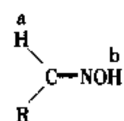
(a) 1.26
(b) 3.27



(a) 1.5
(b) 3.0
(c) 5.5
(d) 5

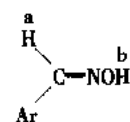


(a) 2.78
(b) 5.16
(c) 4.14
(d) 1.23



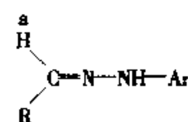
(a) 6.8 ~ 7.9
(b) 7 ~ 10

$\delta_{a\ syn} > \delta_{a\ anti}$



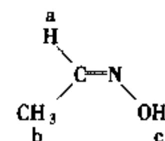
(a) 7.2 ~ 8.6
(b) 7 ~ 10

$\delta_{a\ syn} > \delta_{a\ anti}$

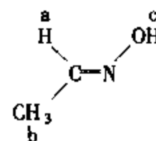


(a) 6.1 ~ 7.7

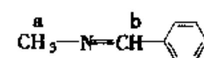
$\delta_{a\ syn} > \delta_{a\ anti}$



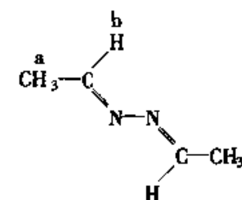
(a) 6.8
(b) 1.9
(c) 9



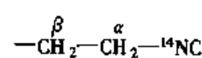
(a) 7.4
(b) 1.9
(c) 9



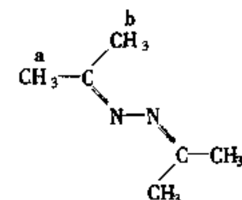
(a) 3.4
(b) 8.40



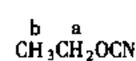
(a) 2.03
(b) 7.89



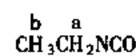
$|J|_{H\alpha N} = 1.8 \sim 2.8$
$|J|_{H\beta N} = 2.5 \sim 3.5$



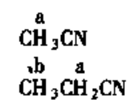
(a) 2.00
(b) 1.83



(a) 4.54
(b) 1.45

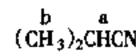


(a) 3.37
(b) 1.20

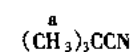


(a) 1.98

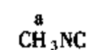
(a) 2.35
(b) 1.31



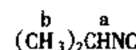
(a) 2.67
(b) 1.35



(a) 1.37



(a) 2.85



(a) 4.83
(b) 1.45

第三节 含 N,S 化合物的 ^{1}H-NMR 化学位移

一、胺类化合物的 ^{1}H-NMR 化学位移

(一) 脂肪胺的 ^{1}H-NMR 化学位移[66]

化合物	化学位移	化合物	化学位移
R—NH$_2$ (a)；R$_2$—NH (a)	(a) 0.5～4.0	R—NH$_3^+$ (a)；R$_2$—NH$_2^+$ (a)；R$_3$—NH$^+$ (a)	(a) 6～9
C$_6$H$_5$—NH$_2$ (a)；C$_6$H$_5$—NH(a)—R；C$_6$H$_5$—NH(a)—C$_6$H$_5$	(a) 2.5～5.0	C$_6$H$_5$—NH$_3^+$ (a)；C$_6$H$_5$—NH$_2^+$(a)—R；C$_6$H$_5$—NH$^+$(a)—R$_2$	(a) 6～9
CH$_3$NH$_2$ (a: CH$_3$)	(a) 2.47	(CH$_3$)$_2$NH (a: CH$_3$)	(a) ≈2.3
CH$_3$CH$_2$NH$_2$ (b: CH$_3$, a: CH$_2$)	(a) 2.74 (b) 1.10	CH$_3$—NH—C$_6$H$_{11}$ (a: CH$_3$)	(a) 2.44
(CH$_3$)$_2$CHNH$_2$ (b: CH$_3$, a: CH)	(a) 3.07 (h) 1.03	CH$_3$—NH—C$_6$H$_5$ (a: CH$_3$, b: NH)	(a) 2.78 (b) 3.55
(CH$_3$)$_2$—N—C$_6$H$_{11}$ (a: CH$_3$)	(a) 2.25	CH$_3$NH—C$_6$H$_4$—NO$_2$ (a: CH$_3$, b: NH)	(a) 2.93 (b) 4.62
CH$_3$—N(哌啶) (a: CH$_3$)	(a) 2.21	(CH$_3$)$_4$N$^+$ (a: CH$_3$)	(a) 3.3
(CH$_3$)$_2$—N—C$_6$H$_5$ (a: CH$_3$)	(a) 2.85	(CH$_3$CH$_2$)$_4$N$^+$ (b: CH$_3$, a: CH$_2$)	(a) 3.25 (b) 1.25
(CH$_3$)$_2$—N—C$_6$H$_4$—NO$_2$ (a: CH$_3$)	(a) 3.09	(CH$_3$)$_3$N$^+$—C$_6$H$_5$ (a: CH$_3$)	(a) 3.72

(二) 脂环胺的 ^{1}H-NMR 化学位移[66]

化合物	化学位移
氮丙啶 (N—Ha, ring CH$_2$ b)	(a) 0.9 (b) 1.61
1,4-二氢吡啶 (N—H; a, b, c)	(a) 5.73 (b) 4.42 (c) 3.15
1,2,3,6-四氢吡啶 (N—Ha; b, c, d, e, f)	(a) 1.63 (b) 2.95 (c) 2.07 (d)(e) 5.72 与 5.77 (f) 3.33
氮杂环丁烷 (N—Ha; b, c)	(a) 2.38 (b) 3.54 (c) 2.23
吗啉 (N—Ha; b, c)	(a) 1.92 (b) 2.87 (c) 3.67
N-甲基哌嗪 (N—Ha; b, c; CH$_3$d)	(a) 2.12 (b) 2.88 (c) 2.37 (d) 2.27
哌啶 (N—Ha; b, c, d)	(a) 1.84 (b) 2.74 (c) 1.5 (d) 1.5
吡咯烷 (N—Ha; b, c)	(a) 2.01 (b) 2.75 (c) 1.59
N-甲基吗啉 (N—CH$_3$; a, b)	(a) 2.32 (b) 3.62

二、硝基化合物的[1]H-NMR 化学位移

(一) 脂肪硝基化合物的[1]H-NMR 化学位移

化合物	化学位移
$\overset{a}{CH_3}NO_2$	(a) 4.29
$\overset{b}{CH_3}\overset{a}{CH_2}NO_2$	(a) 4.37 (b) 1.58
$\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CH_2}NO_2$	(a) 4.28 (b) 2.01 (c) 1.03
$(\overset{b}{CH_3})_2\overset{a}{CH}NO_2$	(a) 4.44 (b) 1.53
$(\overset{a}{CH_3})_3CNO_2$	(a) 1.59

NO_2—CH_2 4.3—CH_2 2.0—CH_2—CH_2 ≈1.4—CH_3 0.9

(二) 脂肪亚硝基及偶氮化合物的[1]H-NMR 化学位移[66]

化合物	化学位移
$(\overset{a}{CH_3})(\overset{b}{CH_3})\overset{+}{N}$=N—$O^-$	(a) 2.96 (b) 3.76
$(\overset{b}{CH_3})_2\overset{a}{CH}$, $(\overset{d}{CH_3})_2\overset{c}{CH}$ $\overset{+}{N}$=N—O^-	(a) 4.89 (b) 1.15 (c) 4.26 (d) 1.52

$\delta_{cis} < \delta_{trans}$(在 α-CH_3—,α-CH_2—及 β-CH_3—系中)

$\delta_{cis} > \delta_{trans}$($\alpha$-CH—)

化合物	化学位移
$\overset{a}{CH_3}$—N=N—CH_3	(a) 3.7
$\overset{a}{CH_3}$—N(→O)=N—$\overset{b}{CH_3}$	(a) 4.16 (b) 3.16
$\overset{a}{CH_3}$—N=N—C_6H_5	(a) 3.4
$(\overset{a}{CH_3})_3C$—N(→O)=N—$\underset{b}{C(CH_3)_3}$	(a) 1.48 (b) 1.28

三、含硫化合物的[1]H-NMR 化学位移和偶合常数

(一) 脂肪硫醇及硫醚的[1]H-NMR 化学位移

化合物	化学位移
R—$\overset{a}{SH}$	(a) 1~2
C_6H_5—$\overset{a}{SH}$	(a) 2~4

Compound	δ	Compound	δ
$\overset{a}{CH_3}SH$	(a) 2.00	$(\overset{c}{CH_3})_2\overset{b}{CH}\overset{a}{SH}$	(a) 1.56 (b) 3.16 (c) 1.34
$\overset{b}{CH_3}\overset{a}{CH_2}SH$	(a) 2.44 (b) 1.31	$(\overset{a}{CH_3})_3CSH$	(a) 1.43
$\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CH_2}SH$	(a) 2.46 (b) 1.57 (c) 1.02	$HSCH_2\overset{c}{CH_2}\overset{b}{CH_2}\overset{a}{SH}$	(a) 1.35 (b) 2.68 (c) 1.88
$\overset{a}{CH_3}SR$	(a) 2.09	$\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CH_2}SR$	(a) 2.43 (b) 1.59 (c) 0.98
$\overset{a}{CH_3}S-C=C$	(a) 2.25	$(\overset{b}{CH_3})_2\overset{a}{CH}SR$	(a) 2.93 (b) 1.25
$\overset{a}{CH_3}S-C_6H_5$	(a) 2.47	$(\overset{a}{CH_3})_3CSR$	(a) 1.39
$\overset{b}{CH_3}\overset{a}{CH_2}SR$	(a) 2.49 (b) 1.25		

（二）脂环硫醚的^{1}H-NMR 化学位移和偶合常数[66]

S, a: (a) 2.27

S, a, b, c: (a) 2.52; (b), (c) 1.6~1.8

S, a, b, O: (a) 7.89; (b) 7.09

S, a, b: (a) 3.21; (b) 2.94

S, a, b, c, d, e: (a,e) 5.97; (b,d) 5.55; (c) 2.84; $J_{ab}=10.0$; $J_{bc}=3.9$; $J_{ac}=1.1$; $J_{bd}=0.0$; $J_{ae}=2.9$; $J_{ad}=0.0$

S, a, b: (a) 2.75; (b) 1.88

S, a, b, c, d, e: (a) 3.19; (b), (c), (d), (e) 5.5~6.2

O, O, S, a, b, c, d, e: (a) 4.00; (b), (c), (d), (e) 6.3~6.7

S, a, b: (a) 3.67; (b) 5.81

S, S, a, b: (a) 2.7; (b) 1.9

S, S, S, a: (a) 4.2

S, a, b, c, d: (a) 3.08; (b) 2.62; (c) 5.48; (d) 6.06; $J_{ab}=9.2$; $J_{bc}=2.5$; $J_{cd}=6.1$; $J_{bd}=2.2$

S, O, a, b: (a) 2.57; (b) 3.88

O, O, S, a, b: (a) 3.74; (b) 6.08

(三) 其他脂肪硫化合物的[1]H-NMR 化学位移和偶合常数

化合物	化学位移
$\overset{a}{C}H_3SSR$	(a) 2.30
$\overset{b}{C}H_3\overset{a}{C}H_2SSR$	(a) 2.67 (b) 1.35
$\overset{a}{C}H_3SOCH_3$	(a) 2.50
$\overset{a}{C}H_3SO_2CH_3$	(a) 2.84
$\overset{a}{C}H_3SO_2\overset{b}{C}H_2\overset{c}{C}H_3$	(a) 2.80 (b) 2.94 (c) 1.47
$\overset{a}{C}H_3SON(\overset{b}{C}H_3)_2$	(a) 2.50 (b) 2.68
$\overset{a}{C}H_3SO_2—OR$	(a) 3.0
$\overset{a}{C}H_3SO_2NH—C_6H_5$	(a) 2.82
$\overset{a}{C}H_3SO_2Cl$	(a) 3.6
$RSO_2O\overset{a}{H}$ $C_6H_5—SO_2O\overset{a}{H}$	(a) 11 ~ 12
$\overset{a}{C}H_3OSO—OCH_3$	(a) 3.58
$\overset{a}{C}H_3OSO_2—OCH_3$	(a) 3.94
$\overset{a}{C}H_3CO\overset{b}{S}H$	(a) 2.4 (b) 4.7
$\overset{a}{C}H_3COS\overset{b}{C}H_3$	(a) 2.30 (b) 2.27

化合物	化学位移
$\overset{c}{C}H_3\overset{b}{C}H_2\overset{a}{C}H_2SSR$	(a) 2.63 (b) 1.71 (c) 1.03
$(\overset{a}{C}H_3)_3CSSR$	(a) 1.32
$\overset{a}{C}H_3SO_2\overset{b}{C}H=\overset{c}{C}H_2$	(a) 2.62 (b) 6.70 (c) *cis* 6.13, *trans* 5.95
$(\overset{a}{C}H_3)_3CSO_2C(OH_3)_3$	(a) 1.44
环状结构（O, S, O; O, a, b, c）	(a) 3.19 (b) 2.44 (c) 4.27
环状结构（O, S, O; a, b）	(a) 3.00 (b) 2.23
环状结构（O, S, O; O, O, a）	(a) 4.68
环状结构（O, S; a, b, c, d）	(a) 2.1 (b) 6.9 (c) 6.4 (d) 7.7
环状结构（S, O; a, b, c）	(a) 6.47 $J_{ab}=5.9$ (b) 7.84 $J_{ac}=2.0$ (c) 4.29 $J_{bc}=2.8$

第四节　脂环及含双键化合物的^{1}H-NMR 化学位移和偶合常数

一、三元环化合物的^{1}H-NMR 化学位移和偶合常数[66]

表 4-16　环丙烷衍生物的^{1}H-NMR 化学位移和偶合常数(一)[8,9]

R	δ_1	δ_2	δ_3	J_{12}	J_{24}	J_{35}	J_{13}	J_{25}	J_{23}
H	0.22			8.97			5.58		4.34
F	4.321	0.270	0.691	5.89	10.80	12.01	2.39	7.70	-6.69
Br	2.84	1.00	0.88	7.3	10.3	10.0	3.9	6.6	-5.9
I	2.93	0.48	0.83	7.51	9.78	9.98	4.37	6.65	-5.93
OH	3.353	0.341	0.587	6.19	10.27	10.88	2.94	6.84	-5.43
COOH	1.58	0.97	1.06	8.0	10.5	11.0	4.6	7.5	-4.3
Li	-2.528	0.434	-0.124	11.8	3.0	3.0	9.5	1.5	-0.5
	2.55	0.91	1.13	8.4	19.1	10.2	3.7	4.0	-7.8
	2.53	0.86	1.10	9.2	11.2	19.6	5.4	2.3	-8.4

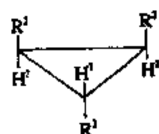
表 4-17　环丙烷衍生物的^{1}H-NMR 化学位移和偶合常数(二)[10]

R	R′	δ_{H_1}	δ_{H_2}	J_{cis}	J_{trans}	J_{gem}
CH_3	CH_3	0.2		9.2	5.4	-4.5
Cl	Cl	1.47		11.2	8.0	-6.0
C_6H_5	Br	0.88	1.17	10.5	7.0	-5.9
C_6H_5	COOH	1.24	1.65	9.6	6.9	-4.0

表 4-18　环丙烷衍生物的^{1}H-NMR 化学位移和偶合常数(三)[11]

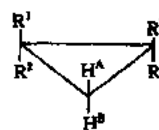
R	R′	δ_A	δ_B	δ_C	$\delta_{C'}$	$J_{AC'}$	J_{BC}	J_{AC}	J_{BC}	$J_{CC'}$	J_{AB}
COCl	COCl	1.82		2.83		9.1		5.9			
$COOCH_3$	$COOCH_3$	1.33		2.03		8.8		6.6			
CN	CN	1.58		2.06		10.2		5.5			
CH_2I	CH_2I	0.79		1.20							
COOEt	C_6H_5	1.110	1.445	1.794	2.388	7.58	8.36	3.8	4.54	4.34	-7.93
CN	C_6H_5	1.252	1.343	1.506	2.430	9.36	7.03	3.69	5.85	5.77	-5.81
Br	$CH=CH_2$	1.21	1.10	2.73	1.82	9.52	7.58	4.36	6.44	3.40	-6.44
$-C_6H_4-CH_3$	COOH	1.30	1.48	2.44	1.84						
$-C_6H_4-NO_2$	COOH	1.47	1.59	2.58	2.05						
Br	Br	1.47		3.10			6.5				
I	I	1.35		2.73							

表 4-19 环丙烷衍生物的^{1}H-NMR 化学位移和偶合常数(四)[12,13]



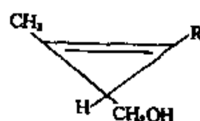
R^1	R^2	R^3	δ_1	δ_2	δ_3	J_{12}	J_{13}	J_{23}
$-C_6H_4-OCH_3$	$COOCH_3$	$COOCH_3$	3.1	2.27	2.27	≈7	≈7	
$COOCH_3$	$-C_6H_4-OCH_3$	$COOCH_3$	≈2.8	≈2.8	≈2.8			
$-C_6H_4-OCH_3$	$COOCH_3$	$COOCH_3$	3.16	2.38	2.38	≈7	≈7	
COPh	COPh	$-CO-C_6H_4-CH_3$	4.20	3.73	3.73	5.6	5.6	
COPh	COPh	$-CO-C_6H_4-NO_2$	4.191	3.693	3.869	5.72	5.60	9.22
COPh	COPh	$-CO-C_6H_4-Br$	4.29	3.772	3.661	5.71	5.67	9.53
COPh	COPh	$-COCMe_3$	4.023	3.571	3.362	5.8	5.4	9.7
COPh	COCOOEt	COCOOEt	3.76	2.70	2.70	5.6	5.6	

表 4-20 环丙烷衍生物的^{1}H-NMR 化学位移和偶合常数(五)[14,15]



R^1	R^2	R^3	R^4	δ_A	δ_B	J_{AB}
CH_3	CN	Cl	$COOCH_3$	0.89	2.09	−7.02
CH_3	CN	COOMe	Cl	1.45	1.64	−7.06
COOH	Cl	CH_3	COOH	1.80	2.11	−6.44
Cl	COOH	CH_3	COOH	1.21	2.27	−6.39
Cl	$COOCH_3$	CH_3	$COOCH_3$	0.99	2.23	−6.52
				0.53	−0.46	−4.50
				0.66	−0.06	−4.65

表 4-21 环丙烷衍生物的^{1}H-NMR 化学位移和偶合常数(六)[16~20]



R	δ	溶 剂
$C(CH_3)_3$	1.66	CCl_4
CH_3	1.38	CCl_4
C_2H_5	1.44	CCl_4

R	δ_A	δ_B	δ_X	J_{AB}	J_{AX}	J_{BX}
H	2.54				3.2	4.5
CH_3	2.28	2.59	2.85	5.37	2.57	3.88
C_2H_5	2.34	2.70	2.80			
				5.6	2.9	
CH_2Cl	2.65	2.84	3.20	5.0	2.4	4.0
ph	2.55	2.93	3.75	5.75	2.5	3.95
CHO	3.10	3.17	3.36	5.54	2.09	4.87
CN	3.11	3.02	3.50	5.53	2.53	4.23

R	δ_1	δ_2	δ_P	J_{11}	J_{22}	J_{gem}
C_2H_5	1.67	0.99				
ph			1.89	6.0	3.1	0.6
CH_2ph	1.69	1.02				

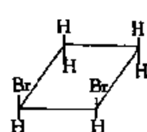
R	R′	R″	δ_A	δ_B δ_X	J_{AB}
H	ph	CH_3	1.62	2.62	2.8
H	ph	C_2H_5	1.60	2.75	
环己烷—CO—		H_2	2.83	←2.26→	

二、四元环化合物的^{1}H-NMR化学位移和偶合常数

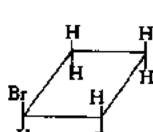
[21 ~ 24]

X	δ_X	δ_A	δ_B	δ_C	δ_D	J_{AB}	J_{AC}	J_{AD}	J_{CD}	$J_{AA'}$	$J_{AB'}$	$J_{BB'}$	J_{DX}	J_{CX}
CH_2		1.96				-11 ~ -15								
C=O		3.03		1.96		-17.54	10.03	6.34	-11.06	4.17	-2.99			
$C=CH_2$		2.7		1.92										
CH_XOH	4.15									-0.01	-0.93	5.16	0.01	-1.07
O						-9.5				0.20	0.14			
S										1.20	-0.20			
N						-6.5								
+NR						-3.0								
CH_XBr	4.51													
CH_XCH_2OH	2.15	1.90		1.90										

[25]

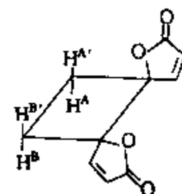


$\delta_{CH}=4.70$
$\delta_{CH_2}=2.60$



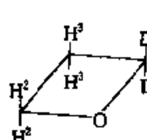
$\delta_{CH}=4.47$
$\delta_{CH_2}=2.60$

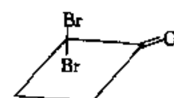
[26]



$J_{AA'}=-12.15$
$J_{BB'}=-12.15$
$J_{AB}=10.19$
$J_{A'B}=10.72$
$J_{AB'}=2.24$
$J_{A'B'}=10.19$

[27]

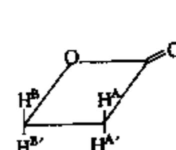




$J_{33}=\mp 11.15$
$J_{44}=\mp 6.02$
$J_{34}=\mp 6.87,\ \mp 8.65$

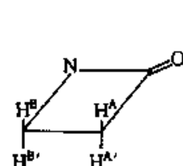
$J_{vic}=7.67, 11.16$
$J_{gem}=-10.92, -15.31$

[28]



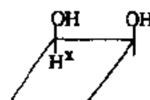
$J_{AB}=6.93$ $J_{AB'}=4.61$
$J_{AA'}=-16.40$ $J_{BB'}=-5.00$

[29]

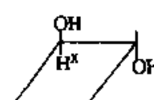


$J_{AA'}=14.2\sim-15.0$
$J_{BB'}=-5.5\sim-5.6$

[30]

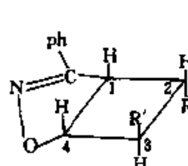


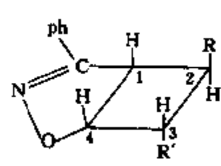
$\delta_X=3.70$



$\delta_X=3.50$

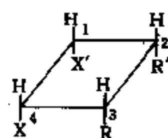
[31]





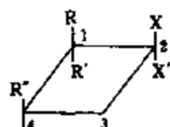
R	R'	$^4J_{1,3trans}$	$^4J_{2,4cis}$	R	R'	$^4J_{2,4trans}$	$^4J_{1,3cis}$
Cl	Cl	−1.49	1.23	Cl	Cl	−0.91	2.42
Br	Br	−1.38	1.21	Br	Br	−0.61	2.48
Cl	OH	−1.55	1.42				

[32]



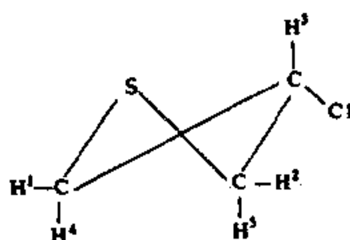
X	X	R	R'	$^4J_{1,3cis}$	$^4J_{2,4cis}$
Cl	Cl	COOH	COOH	1.3	1.3
Cl	Cl	$COOCH_3$	$COOCH_3$	1.4	1.4
Br	Br	$COOCH_3$	$COOCH_3$	1.2	1.2
Cl	Cl	CO—O—CO		1.5	1.5
COONa	O-phONa	COONa	O-phONa	0.6	0.6

[33]



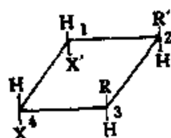
R	R'	X	X'	R''	$J_{3,3'}$	$J_{4,4'}$	J_{34}	J_{trans}
CN	Cl	Cl	CN	H	−13.1	−13.1	9.4	4.5,9.3
Br	$COOCH_3$	$COOCH_3$	Br	H	−12.0	−12.0	6.2	8.4,10.0
CN	CN	CN	CN	OCH_3	−14		(J_{cis} = 7.8,9.2)	
$COOCH_3$	Cl	$COOCH_3$	Cl	$CH=CH_2$	−12.96		11.38	9.52
Cl	COOH	Cl	COOH	$CH=CH_2$	−11.97		10.75	7.68
Cl	$COOCH_3$	Cl	$COOCH_3$	$CH=CH_2$	−11.66		10.81	7.93

[33]



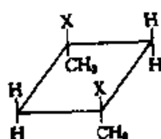
$\delta_1 = 3.31$	$\delta_2 = 3.31$	$\delta_3 = 5.13$	$J_{12} = 3.116$	$J_{13} = 7.670$	$J_{14} = 8.633$
$\delta_4 = 3.66$	$\delta_5 = 3.66$		$J_{15} = -0.751$	$J_{23} = 7.670$	$J_{24} = -0.751$
			$J_{34} = 9.343$	$J_{45} = -0.482$	

[32]



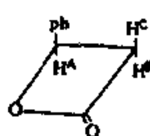
X	X'	R	R'	$^4J_{1,3trans}$	$^4J_{2,4trans}$
Cl	Cl	COOH	COOH	−1.4	−1.4
Cl	Cl	CH_2OH	CH_2OH	−1.5	−1.5
COONa	O-phONa	COONa	O-phONa	−1.1	−1.1

[34]

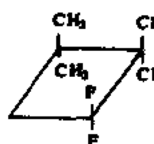


X	异 构 体	δ_{CH_3}	δ_{CH_2}
Br	*cis*	1.88	3.19
Br	*trans*	2.13	3.21
Cl	*cis*	1.69	2.96
Cl	*trans*	1.86	2.88

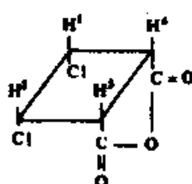
[35,32,36]



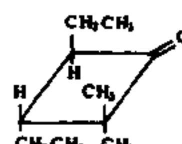
$J_{cis} = 4.9$
$J_{trans} = 5.9$
$J_{gem} = 16.6$



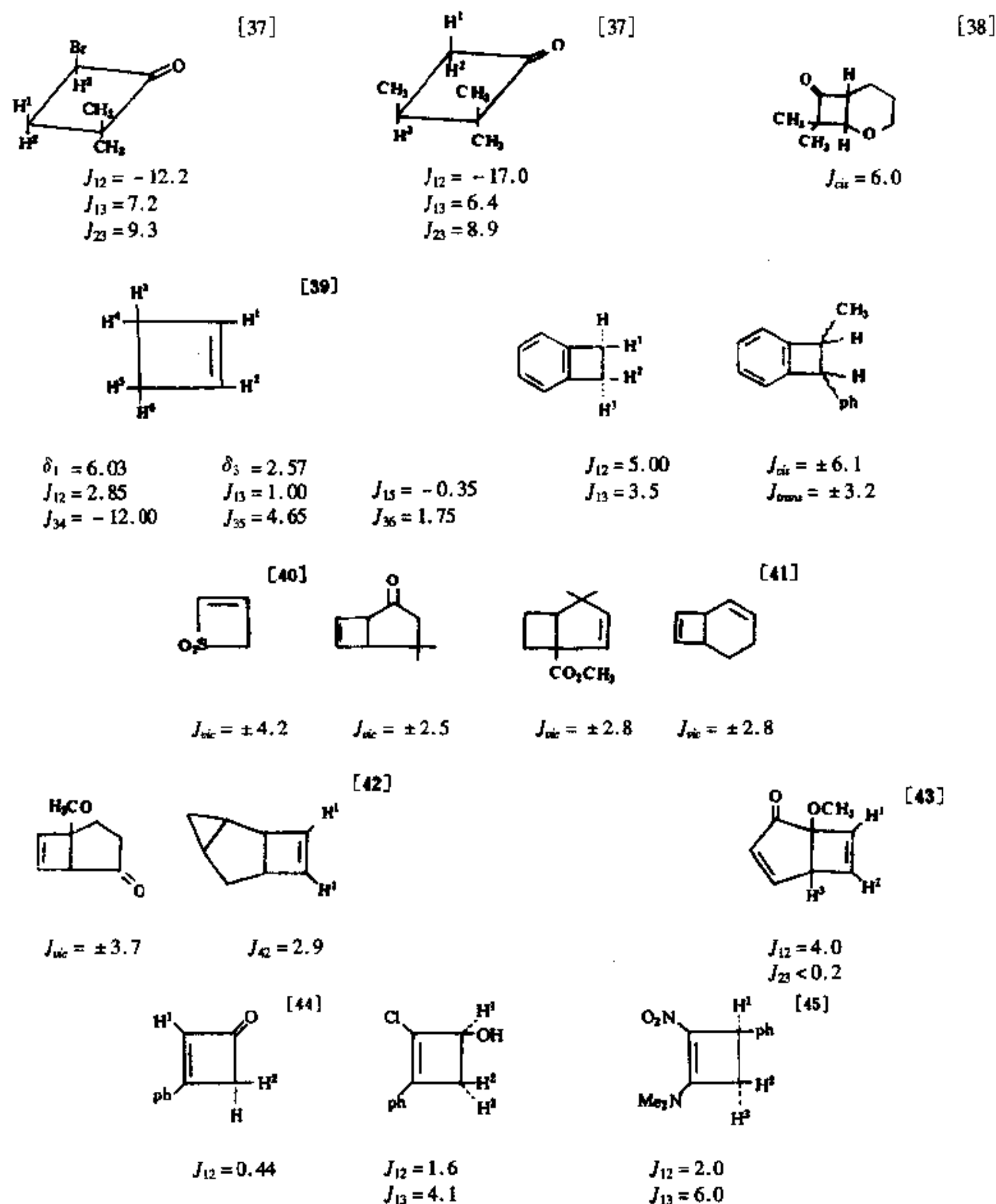
$J_{gem} = -13$



$J_{12} = 6.7$ $J_{13} = 1.5$
$J_{34} = 8.1$ $J_{14} = 8.8$



$J_{vic} = 6.9$



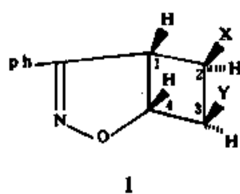
三、五元环衍生物的^{1}H-NMR化学位移和偶合常数

表 4-22 五元环衍生物 1～4 的^{1}H-NMR化学位移和偶合常数

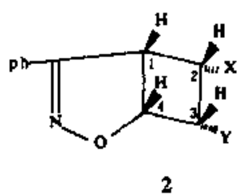
化合物	X	Y	δ_1	δ_2	δ_3	δ_4
1	Cl	Cl	4.468	4.723	4.774	5.331
	CO_2CH_3	CO_2CH_3	4.424	3.596	3.676	5.550
	Br	Br	4.620	4.834	4.892	5.445
2	Cl	Cl	5.3778	5.029	5.396	5.244
3	Cl	Cl	4.786	4.596	4.398	5.090
	Cl	OH	4.774	4.570	4.246	4.972
	Br	Br	4.851	4.728	4.544	5.271
4	Cl	Cl	4.305	4.354	4.710	5.489
	Br	Br	4.488	4.476	4.922	5.466

续表

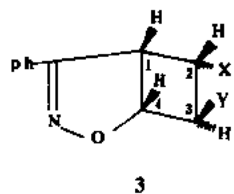
化合物	J_{14}	J_{23}	J_{12}	J_{34}	$^4J_{13}$	$^4J_{24}$
1	8.59±0.04 7.88±0.05 8.49±0.03	6.89±0.05 9.85±0.09 7.28±0.04	2.87±0.07 3.25±0.08 3.26±0.05	4.06±0.06 4.54±0.09 4.29±0.05	-1.66±0.07 -1.44±0.08 -1.77±0.06	-0.68±0.07 -0.94±0.09 -0.73±0.05
2	7.64±0.12	6.79±0.06	7.05±0.06	5.12±0.10	2.16±0.04	2.98±0.04
3	7.75±0.04 7.66±0.04 7.65±0.04	6.71±0.04 6.18±0.04 6.98±0.04	8.30±0.04 8.11±0.04 8.25±0.04	3.68±0.03 3.35±0.04 3.57±0.03	-1.49±0.04 -1.55±0.04 -1.38±0.05	1.23±0.04 1.42±0.04 1.21±0.04
4	7.67±0.10 7.51±0.13	5.05±0.07 5.47±0.10	3.93±0.05 4.01±0.08	6.00±0.05 6.10±0.07	2.42±0.07 2.48±0.10	-0.91±0.05 -0.61±0.13



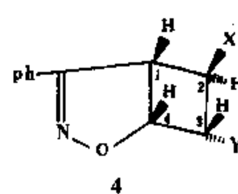
1



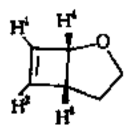
2



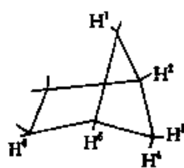
3



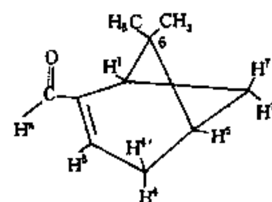
4



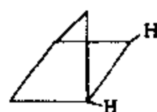
$J_{12}=2.8$
$J_{24}=2.8$
$J_{13}=1.5$



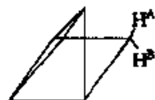
$J_{14}\approx 7$ $J_{23}\approx 2$
$J_{45}\approx 0$ $J_{56}\approx 0$



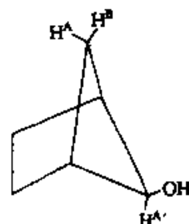
$J_{13}=1.488$ $J_{14}=J_{14'}=0.0$ $J_{15}=5.779$
$J_{17}=0.038$ $J_{17'}=5.394$ $J_{34}=3.012$
$J_{34'}=3.048$ $J_{35}=1.505$ $J_{37}=J_{37'}=0.0$
$J_{44'}=0.060$ $J_{45}=2.771$ $J_{47}=J_{47'}=0.0$
$J_{4'5}=3.066$ $J_{4'7}=J_{4'7'}=0.0$ $J_{57}=0.110$
$J_{57'}=5.747$ $J_{77'}=9.049$



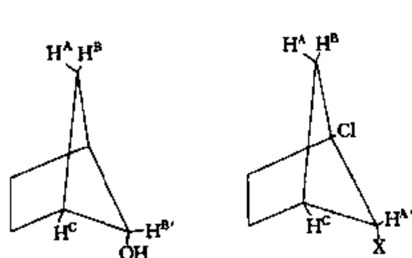
$J=0$

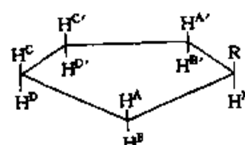


$J_{AB}=-3.1$



$J_{AA'}=6.8$ $J_{AB}=-6.8$
$\delta_B=2.59$



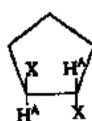


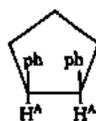
$J_{BC}=2.9$

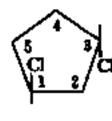
$\delta_C=2.37$

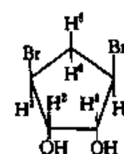
X	J_{AB}	J_{AC}
CO_2CH_3	-6.4	3.3
COCl	-6.6	
CO_2H	-6.6	

R	δ_X	δ_A	δ_C
H	1.51		
OH	4.18		
NH_2	3.25		
$NHCH_3$	2.98		
R	δ_X	δ_A	δ_C
$N(CO)_2C_6H_4$	4.70		
Cl	4.36	≈1.86	≈1.86
Br	4.37	1.95	1.95
I	4.36	≈1.91	≈1.91









X	δ_A
ph	1.2
Cl	4.30
Br	4.58

$\delta_A=0.9$

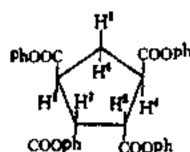
$\delta_2=2.43$

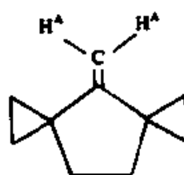
$\delta_1=4.14$　$\delta_2=4.37$

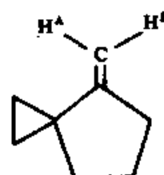
$\delta_5=2.34$　$\delta_6=3.22$

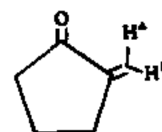
$J_{56}=14.9\sim15.0$　$J_{16}=7.6$

$J_{15}=6.1$　$J_{12}=4.5$









$\delta_1=5.72$　$\delta_2=6.03$

$\delta_5=2.12$　$\delta_6=3.30$

$J_{56}=15.6$　$J_{16}=7.6$

$J_{15}=2.8$　$J_{12}=4.7$

$\delta_A=3.88$

$\delta_A=4.16$

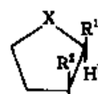
$\delta_B=4.46$

$\delta_A=5.72$

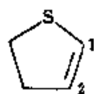
$\delta_B=5.04$



或



X	R^1	R^2	δ_1	δ_2	δ_4
O	H	H	3.75	1.85	
O	CH_3	H	3.55		
NH	H	H	2.74	1.62	
NH	=O	H		2.23	3.37
S	H	H	2.82	1.93	
SO_2	H	H	2.92	2.16	

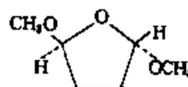


$J_{12} = 5.57$



$\delta_1 = 6.23$ $\delta_2 = 4.86$

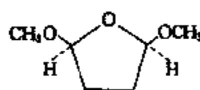
$\delta_3 = 3.75$ $J_{12} = 2.43$



$\delta_{CH_2} = 1.7 \sim 2.1$

$\delta_{CH} = 4.98$

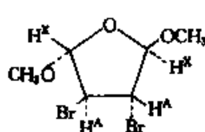
$\delta_{CH_3} = 3.28$



$\delta_{CH_2} = 1.91$

$\delta_{CH} = 4.95$

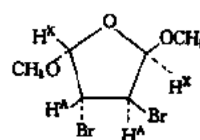
$\delta_{CH_3} = 3.31$



$\delta_A = 4.10$

$\delta_X = 5.20$

$\delta_{CH_3} = 3.47$



$\delta_A = 4.36$

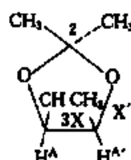
$\delta_X = 5.16$

$\delta_{CH_3} = 3.44$



$\delta_2 = 4.57$

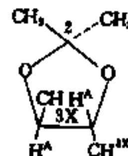
$\delta_4 = 3.57$



$\delta_{CH_3}{}^{(C_2)}$ 1.33, 1.22

δ_{HX} 1.05

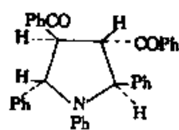
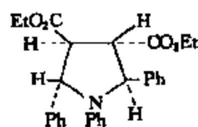
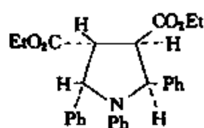
δ_{HA} 4.15

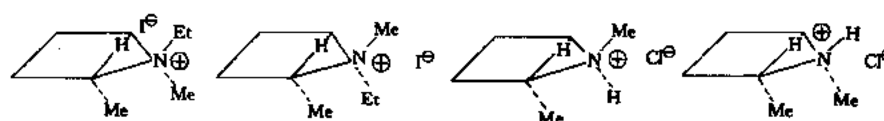


$\delta_{CH_3}{}^{(C_2)}$ 1.28, 1.28

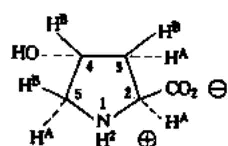
δ_{HX} 1.15

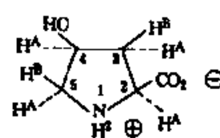
δ_{HA} 3.38

	δ_2	δ_3	δ_4	δ_5
	5.70	4.69	4.73	5.60
	5.78	3.57	3.57	5.78
	5.62	3.69	3.69	5.90

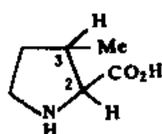


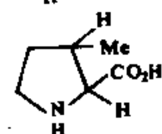
$\delta_{N-Me}=2.98$　　$\delta_{N-Me}=3.28$　　$\delta_{N-Me}=3.03$　　$\delta_{N-Me}=2.73$



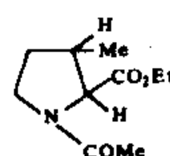


$\delta_{2A}=4.17$	$\delta_{4B}=4.48$	$\delta_{2A}=4.04$	$\delta_{5A}=3.19$
$\delta_{3A}=2.30$	$\delta_{5A}=3.17$	$\delta_{3A}=2.31$	$\delta_{5B}=3.25$
$\delta_{3B}=1.95$	$\delta_{5B}=3.31$	$\delta_{3b}=2.05$	
		$\delta_{4A}=4.40$	

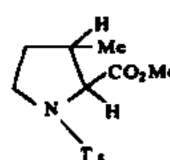




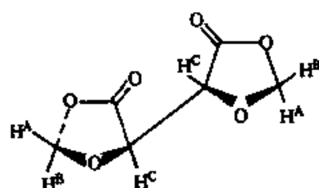
	δ_{CH_3}	δ_{H^2}
顺	1.00	4.08
反	1.22	3.32



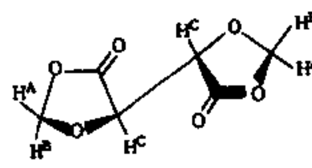
顺	1.05	4.41
反	1.18	3.96



顺	0.86	4.17
反	0.86	—



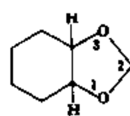
(Ⅰ)



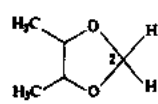
(Ⅱ)

		δ_A	δ_B	δ_C
(Ⅰ)	CCl_4	4.46	4.48	5.46
	$CDCl_3$	4.35	4.41	5.27
	C_6H_6	5.32	5.52	6.02
	$\Delta^{C_6H_6}_{CCl_4}$	+0.86	+1.04	+0.56

		δ_A	δ_B	δ_C
(Ⅱ)	CCl_4	4.45	4.49	5.42
	$CDCl_3$	4.40	4.44	5.29
	C_6H_6	5.20	5.52	6.07
	$\Delta^{C_6H_6}_{CCl_4}$	+0.75	+1.03	+0.55

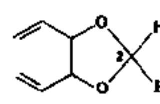


$\delta_2=5.05$



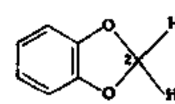
内消旋体：$\delta_2=4.7,4.99$

外消旋体：$\delta_2=4.85$



$\delta_2=4.15,4.83$

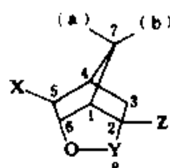
$\delta_2=4.99$



$\delta_2=6.00$

四、六元环衍生物的^{1}H-NMR化学位移和偶合常数

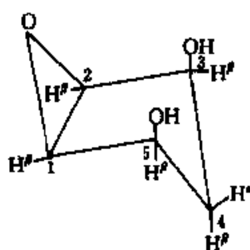
表 4-23 六元环衍生物的^{1}H-NMR化学位移数据(一)[46,47]

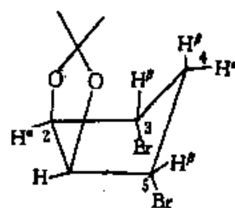


X	Y	Z	δ_1	δ_{6exo}	δ_{5endo}	δ_4	δ_{3exo}	δ_{3endo}	δ_{2exo}	δ_{7a}	δ_{7b}	J_{43exo}	J_{2exo4}
I	C═O	H	3.22	5.12	3.92	2.70	2.06	1.52	2.54	2.32	1.82		
Br	C═O	H	3.25	4.94	3.87	2.65	2.11	1.75	2.52	2.28	1.74	10.5	≈5
AcO	C═O	H	3.20	4.49	4.55	2.50	2.03	1.72	2.55	1.99	1.62		
TsO	C═O	H	3.13	4.48	4.25	2.49	1.96	1.57	2.40	1.98	1.57		
I	C═O	CH_3	2.78	5.07	3.85	2.66	1.52	1.94	1.17(CH_3)	2.36	1.88		
Br	C═O	CH_3	2.80	4.85	3.79	2.50	1.59	1.81	1.16(CH_3)	2.29	1.76		
TsO	CH_2	CH_3	2.72	4.80	4.08	2.32	1.86	1.89	2.34	2.05	1.87		
AcO	CH_2	CH_3	2.62	4.06	4.32	2.22	1.85	1.96	2.31	2.08	1.86		

X	Y	Z	$J_{2exo6exo}$	$J_{6exo5endo}$	J_{7a4}	J_{3exo4}	J_{3endo4}	J_{7b4}	$J_{3exo3endo}$	J_{7a7b}	J_{8a8b}	J_{16exo}	J_{12exo}	J_{5endo4}
I	C═O	H			1.8	3.6	0.5	1.5	13.4	11.2		5.4	5.0	0.5
Br	C═O	H	≈5	0.3	1.4	3.8	0.8	1.5	13.2	11.4		5.0	4.9	0.5
AcO	C═O	H				3.8			13.0	11.0		4.6	4.6	0.8
TsO	C═O	H				4.0			13.4	11.0		4.8	5.0	1.1
I	C═O	CH_3			1.6	4.7	0.7	1.6	13.6	11.1		5.1		1.0
Br	C═O	CH_3			1.6	4.1	0.8	1.3	13.6	11.1		5.0		0.6
TsO	CH_2	H				4.7			13.0	10.6	8.2			
AcO	CH_2	H			1.7			1.4	13.2	10.6	8.2	5.2	4.0	1.1

X	Y	Z	$J_{3endo2exo}$	$J_{3exo2exo}$	J_{7a1}	J_{7b1}	J_{8a2exo}	J_{6exo4}	J_{3exo1}	$J_{7b5endo}$	$J_{7a3endo}$	J_{2bexo}	J_{24}	J_{14}
I	C═O	H	3.0	10.2	1.6	0.6		1.0	0.5	2.6	1.3	1.2	0.6	1.4
Br	C═O	H	2.0	10.6	1.4	1.5		1.0	0.3	2.4	2.0	1.0		1.6
AcO	C═O	H		10.5	1.5	1.6		1.2	0.3	1.7		1.2		1.2
TsO	C═O	H		10.3	1.8	1.8		1.1		1.7		1.1		1.0
I	C═O	CH_3			1.4	1.6			0.8	2.1	2.1			1.4
Br	C═O	CH_3			1.4	1.3		1.0		2.1	1.9			1.4
TsO	CH_2	H	2.6	10.8			3.6				2.2			
AcO	CH_2	H	2.2	10.0	1.7	1.4	3.6			1.8	2.2	1.0		





$\delta_1=3.33$　$\delta_3=3.91$　$\delta_{4\alpha}=1.13$　$\delta_4=5.01$　$\delta_3=4.27$　$\delta_{4\alpha}=2.46$

$\delta_{4\beta}=1.86$　$J_{4\alpha4\beta}=-12.0$　$J_{3\beta4\beta}=7.5$　$\delta_{4\beta}=3.12$　$J_{4\alpha4\beta}=-16.1$　$J_{3\beta4\beta}=6.2$

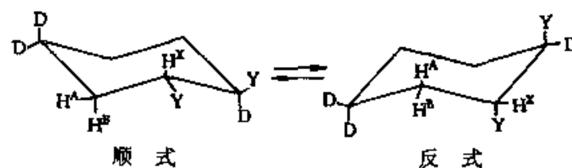
$J_{3\beta4\alpha}=8.8$　$J_{15}=0.5$　$J_{14\beta}=0.5$　$J_{3\beta4\alpha}=3.2$　$J_{15}=0.8$　$J_{11\alpha}=0.9$

表 4-24 六元环衍生物的^{1}H-NMR 化学位移数据(二)[66]

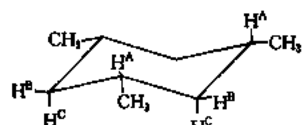
取代基 X	化学位移 H_{ax}	化学位移 H_{eq}	取代基 X	化学位移 H_{ax}	化学位移 H_{eq}
-D	1.12	1.60	-OH	3.38	3.89
$-CH_3$	1.27	1.93	$-OCOCH_3$	4.46	4.98
-Ph	2.47	2.98	$-NH_2$	2.52	3.15
-Cl	3.63	4.34	$-NHCH_3$	2.08	2.70
-Br	3.81	4.62	$-NO_2$	4.23	4.43
-I	3.98	4.72	-SH	2.57	3.43

表 4-25 六元环衍生物的^{1}H-NMR 化学位移数据(三)[66]

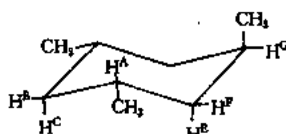
取代基 X		化学位移 H_{1ax}或H_{1eq}	H_{2ax}	H_{2eq}	H_{3ax}	H_{3eq}	H_{4ax}	H_{4eq}
CH_3	eq	0.15	-0.31	-0.03	0.03	0	-0.06	-0.02
	ax	0.33	0.25	-0.20	0.27	-0.26	-0.06	-0.02
-Cl	eq	2.51						
	ax	2.74			0.6			
-OH	eq	2.26	-0.03	0.18	0.07	0.01	0.01	0.06
	ax	2.29	0.23	-0.02	0.46	-0.27	0.02	-0.08
$-OCOCH_3$	eq	3.34						
	ax	3.38	0.35	≈0.7				
$-NO_2$	eq	3.11	1.1	0.3				
	ax	2.83	0.5	1.0				
-SH	eq	1.45	-0.4	-0.3				
	ax	1.83		-0.1	0.8			



化合物	顺式 δ_A	顺式 δ_B	顺式 δ_X	反式 δ_A	反式 δ_B	反式 δ_X
二乙酰基物	1.80	1.57	4.92	1.41	1.29	4.68
二羟基物	1.77	1.53	3.75	1.92	1.23	3.30
二对甲苯磺酰基物	1.96	1.54	4.51	1.96	1.48	4.40
异丙烯基物	1.81	1.54	3.96	2.05	1.37	3.10
二氯化物				1.99	1.39	3.70
二溴化物				2.10	1.50	4.11
二碘化物				2.00	1.56	4.73

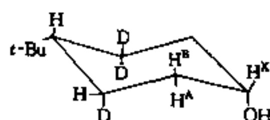


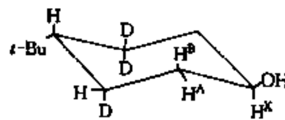
cis, *cis* 异构体



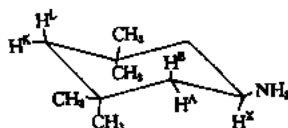
trans, *cis* 异构体

异构体	δ_A	δ_B	δ_C	δ_E	δ_F	δ_G	δ_{CH_3}	J_{AB}	J_{AC}	J_{ACH_3}	J_{AE}	J_{BC}	J_{EF}	J_{EG}	J_{FG}	J_{GCH_3}
顺,顺	1.40	1.64	0.47				0.86	3	11	6.3		13				
反,顺	1.52	1.52	0.47	1.01	1.52	2.00	0.83(e), 0.97(a)		12.0	6.2	12.5	13.5	12.5	4.7	2.3	7.2

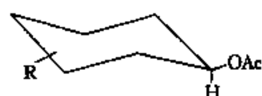


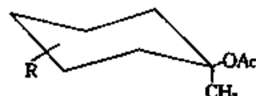


异构体	顺 δ_A	式 δ_B	δ_X	反 J_{AB}	式 J_{BX}	J_{AX}
顺 式	1.84	1.43	4.03		≈2.7	≈2.7
反 式	1.98	1.38	3.51	12.5	11.0	4.2



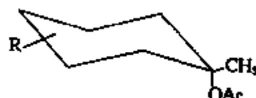
$\delta_{CH_3(ax)} = 0.98$	$\delta_A = 1.56$	$\delta_B = 0.79$	$\delta_K = 1.19$
$\delta_{CH_3(eq)} = 0.88$	$\delta_L = 0.99$	$\delta_X = 2.91$	$J_{AB} \approx 11.5$
$J_{AX} = 3.65$	$J_{BX} = 11.50$	$J_{KL} = 13.8$	$J_{XA} = 1.8$



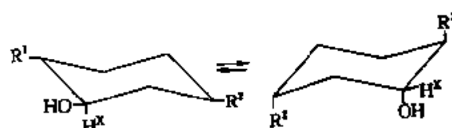


$\delta_{CH_3} = 1.97 \sim 2.12$　　　　$\delta_{CH_3} = 1.88 \sim 1.93$

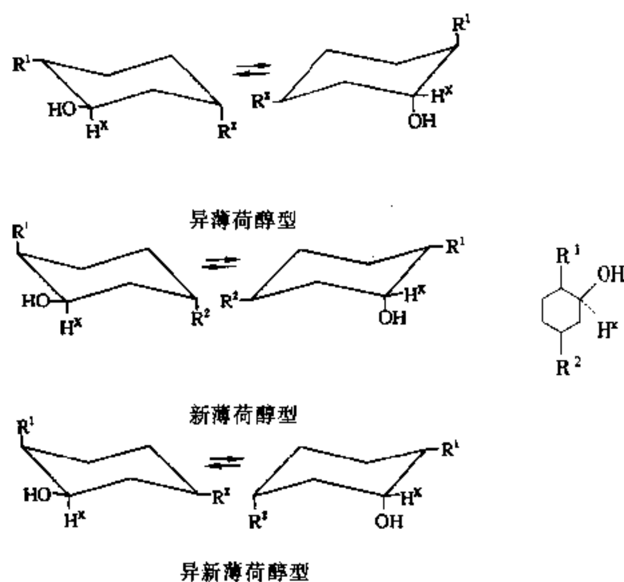




$\delta_{CH_3} = 2.10 \sim 2.20$　　　　$\delta_{CH_3} = 1.96 \sim 2.07$



薄荷醇型



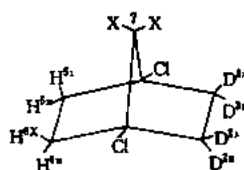
异薄荷醇型

新薄荷醇型

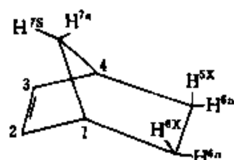
异新薄荷醇型

R^1	R^2	类　型	δ_X	J_{aa}	J_{ea}	J_{ae}	J_{ee}
CH_3	CH_3	薄荷醇型	3.08				
$(CH_3)_2CH$	CH_3	薄荷醇型	3.38	9.4	4.2		
CH_3	$(CH_3)_2CH$	薄荷醇型	2.98				
$(CH_3)_3C$	CH_3	薄荷醇型	3.50	9.4	4.2		
CH_3	CH_3	异薄荷醇型	3.73				
$(CH_3)_2CH$	CH_3	异薄荷醇型	3.75	6.7	5.1		
CH_3	$(CH_3)_2CH$	异薄荷醇型	3.50				
$(CH_3)_3C$	CH_3	异薄荷醇型	3.80	7.6	5.2		
CH_3	CH_3	新薄荷醇型	3.47				
$(CH_3)_2CH$	CH_3	新薄荷醇型	4.05				
CH_3	$(CH_3)_2CH$	新薄荷醇型	3.83			3.0	2.0
$(CH_3)_3C$	CH_3	新薄荷醇型	4.15				
CH_3	CH_3	异新薄荷醇型	3.70	10.5	4.5		
$(CH_3)_2CH$	CH_3	异新薄荷醇型	3.95				
CH_3	$(CH_3)_2CH$	异新薄荷醇型	3.65	10.0	4.6		
$(CH_3)_3C$	CH_3	异新薄荷醇型	4.23			3.6	2.2

五、桥环衍生物的¹H-NMR 化学位移和偶合常数



X	Y	δ_{5n}	δ_{5x}	δ_{7s}	δ_{7a}	J_{5n6n}	J_{5n5x}	J_{5n6x}	J_{5x7a}	J_{5n7s}	J_{5x6x}
OCH_3	OCH_3	1.537	2.174			9.82	−11.78	4.46			12.71
OAc	H	1.541	2.142	5.362		9.15	−12.15	4.16	0.40	1.16	12.85
Cl	Cl	1.431	2.001			9.97	−12.31	4.47			12.50
H	H	1.543	1.790	1.889	1.889	9.15	−12.09	4.74		−2.19	13.20

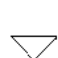
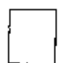
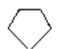


$\delta_2 = 5.93$
$\delta_1 = 2.82$
$\delta_{5x} = 1.59$
$\delta_{5n} = 0.96$
$\delta_{7s} = 1.33$
$\delta_{7a} = 1.06$
$J_{17a} = 1.5$

$J_{17s} = 1.8$
$J_{5n7s} = 2.2$
$J_{27a} \approx 0.5$
$J_{7a7s} = 7.7$
$J_{12} = 2.0$
$J_{23} = 6.0$
$J_{13} = 1.2$

$J_{16n} = 0$
$J_{16x} = 3.5$
$J_{14} = 0$
$J_{5n6n} = 4.4 \sim 5.6$
$J_{5x6x} = 8.0 \sim 9.1$
$J_{5n6x} = 4.4$
$J_{5n5x} = 10.6$

六、其他不同脂环化合物的^{1}H-NMR 化学位移和偶合常数[66]

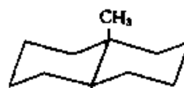
	δ	J
	0.22	$J_{gem} = -3 \sim -9$ $J_{cis} = 7 \sim 13$ $J_{trans} = 4 \sim 9.5$
	1.96	$J_{gem} = -11 \sim -17$ $J_{cis} = 4 \sim 12$ $J_{trans} = 2 \sim 10$ $J = 0.5 \sim 2.0$ （远程偶合）
	1.51	$J_{gem} = -8 \sim -18$ $J_{cis} = 5 \sim 10$ $J_{trans} = 5 \sim 10$
	1.44 (for-100℃: H_{ax}:1.1, H_{eq}:1.6)	$J_{gem} = -11 \sim -14$ $J_{ax,ax} = 8 \sim 13$ $J_{eq,ax} = 2 \sim 6$ $J_{eq,eq} = 2 \sim 5$

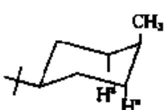


(a) 1.8
(b) 1.9

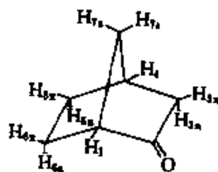


$J_{ac} \approx 7$
$J_{ad} = J_{bd} \approx 0$





甲基信号由于 H^a 的远程偶合明显变宽。

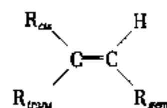


	δ	H	J	H	J
H_1	2.41	1,4	1.2	5n,5x	-12.8
H_{3n}	1.73	1,5n	-0.3	5n,6n	9.1
H_{3x}	1.95	1,5x	0.2	5n,6x	4.7
H_4	2.61	1,6n	0.1	5n,7a	-0.1
H_{5n}	1.41	1,6x	4.7	5n,7s	2.1
H_{5x}	1.76	1,7a	1.2	5x,6n	4.6
H_{6n}	1.44	1,7s	1.6	5x,6x	12.1
H_{6x}	1.76				
H_{7a}	1.51	3n,3x	-17.6	6n,6x	-12.3
H_{7s}	1.69	3n,7a	4.2	6n,7a	-0.1
		3x,4	4.8	6n,7s	2.3
		3x,5x	2.3		
				7a,7s	-10.2
		4,5n	0.1		
		4,5x	4.3		
		4,6n	-0.5		
		4,6x	0.7		
		4,7a	2.1		
		4,7s	1.6		

七、含双键化合物的^{1}H-NMR化学位移

(一) 双键氢化学位移的计算[66]

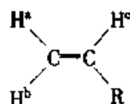
$$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$



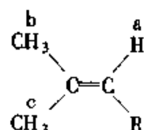
取代基 R	Z_{gem}	Z_{cis}	Z_{trans}	取代基 R	Z_{gem}	Z_{cis}	Z_{trans}
—H	0	0	0	—NHR,R 脂肪	0.80	-1.26	-1.21
—烷烃	0.45	-0.22	-0.28	—NR_2,R 脂肪	0.80	-1.26	-1.21
—环烷烃①	0.69	-0.25	-0.28	—NHR,R 不饱和	1.17	-0.53	-0.99
—CH_2-芳环	1.05	-0.29	-0.32	—NRR',R 不饱和 R'(任意的)	1.17	-0.53	-0.99
—CH_2X,X:F,Cl,Br	0.70	0.11	-0.04				
—CHF_2	0.66	0.32	0.21	—NCOR	2.08	-0.57	-0.72
—CF_3	0.66	0.61	0.32	—N=N—苯环	2.39	1.11	0.67
—CH_2O	0.64	-0.01	-0.02	—NO_2	1.87	1.30	0.62
—CH_2N	0.58	-0.10	-0.08	—SR	1.11	-0.29	-0.13
—CH_2S	0.71	-0.13	-0.22	—SOR	1.27	0.67	0.41
—CH_2CO,CH_2CN	0.69	-0.08	-0.06	—SO_2R	1.55	1.16	0.93
—C=C 孤立	1.00	-0.09	-0.23	—SCOR	1.41	0.06	0.02
—C=C,共轭②	1.24	0.02	-0.05	—SCN	0.80	1.17	1.11
—C≡C	0.47	0.38	0.12	—SF_5	1.68	0.61	0.49
—芳环(自由旋转)	1.38	0.36	-0.07	—CHO	1.02	0.95	1.17
—芳环(旋转受阻)③	1.60	—	-0.05	—CO 孤立	1.10	1.12	0.87
—芳环(邻位有取代基)	1.65	0.19	0.09	—CO 共轭②	1.06	0.91	0.74
—F	1.54	-0.40	-1.02	—COOH 孤立	0.97	1.41	0.71
—Cl	1.08	0.18	0.13	—COOH 共轭②	0.80	0.98	0.32
—Br	1.07	0.45	0.55	—COOR 孤立	0.80	1.18	0.55
—I	1.14	0.81	0.88	—COOR 共轭②	0.78	1.01	0.46
—OR,R(脂肪)	1.22	-1.07	-1.21	—$CONR_2$	1.37	0.98	0.46
—OR,R(不饱和)	1.21	-0.60	-1.00	—COCl	1.11	1.46	1.01
—OCOR	2.11	-0.35	-0.64	—CN	0.27	0.75	0.55
—NH_2	0.80	-1.26	-1.21	—PO$(OCH_2CH_3)_2$	0.66	0.88	0.67
				—OPO$(OCH_2CH_3)_2$	1.33	-0.34	-0.66

① 环烷烃系指取代基与双键形成环状物。
② 系指双键或双键取代基与另外取代基共轭。
③ 形成芳香共轭双键,如1,2-二氢萘。

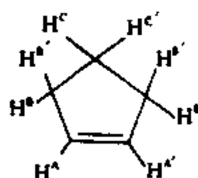
(二) 双键氢的^{1}H-NMR化学位移



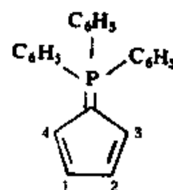
R	δ_a	δ_b	δ_c	R	δ_a	δ_b	δ_c
烷基	4.87~8	4.94~7	5.72~8	$COCH_3$	5.90	6.27	6.30
CH_2X	5.05~17	5.23~9	5.89~6.04	F	4.03	4.37	6.17
CH_2COCH_3	4.98	5.03	5.80	Cl	5.39	5.48	6.26
OR'	3.94	4.15~6	6.42~7	Br	5.97	5.84	6.44
OCOR'	4.51~6	4.84~8	7.27~30	I	6.23	6.57	6.53
(苯环)	5.20	5.72	6.72	CN	6.07	6.20	5.73



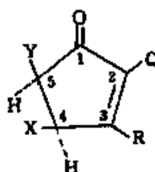
R	δ_a	δ_b	δ_c	R	δ_a	δ_b	δ_c
—H		1.70	1.70	—CHO	5.63	1.91	2.11
—C(CH$_3$)$_3$	5.13	1.68	1.62	—COCH$_3$	5.97	1.86	2.06
—C≡CH	5.17	1.80	1.88	—COOCH$_3$	5.62	1.84	2.12
—Br	5.78	1.75	1.75	—COCl	6.01	1.97	2.12
—OCOCH$_3$	6.79	1.65	1.65				



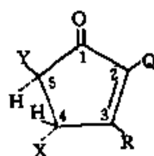
$\delta_A = 5.60$ $\delta_B = 2.28$
$\delta_C = 1.90$ $J_{AB} = 0.5$
$J_{BB'} = -15.3 \sim -18.4$



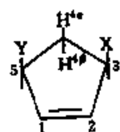
$\delta_1 = 6.28$ $\delta_3 = 6.45$ $J_{12} = 2.80$
$J_{13} = 3.84$ $J_{14} = 1.89$ $J_{34} = 2.16$



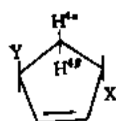
Q	R	X	Y	δ_2	δ_3	δ_4	δ_5	$J_{45,trans}$	J_{45cis}	J_{34}	J_{24}	$J_{55,gem}$	J_{23}
H	H	H	H	3.93	3.19								
H	OCH$_3$	H	CH$_3$	5.28		2.60	2.80						
CH$_3$	OCH$_3$	O O					2.45						
CH$_3$	OCH$_3$	H	H O O			2.81							
H	OCH$_3$	OAc	CH$_3$	5.37		5.86	2.77						
H	OCH$_3$	CH$_3$	OAc	5.28		3.17	5.31						
H	OAc	OAc	CH$_3$	6.37		5.97							
H	OCH$_3$	CH$_2$CH$_3$	H	1.73		2.58	1.92,2.40						
I	OCH$_3$	CH$_3$	H	5.25		2.88	2.38						
CH$_3$	OCH$_3$	OH	H			4.64	2.28,2.96	2.6	6.8			−19.8	
(CH$_2$)$_6$COOCH$_3$	H	OAc	H		7.1	5.65	2.79		6.1	2.6	−1.2	−18.4	
(CH$_2$)$_6$COOCH$_3$	H	OH	H		7.18	4.92	2.29,2.79	2.3	5.7			−18.5	
H	H	OBz	H	6.28	7.58	5.98	2.38,2.83	2.3	6.6	2.7	−1.3	−19	5.7
H	H	Br	H	6.17	7.62	5.15	2.56,2.92	1.8	6.4	2.6, 3.0	−1.2, ±1.3		



Q	R	X	Y	δ_2	δ_4	δ_5
H	OCH_3	OAc	CH_3	5.37	5.43	2.41
H	OAc	OAc	CH_3	6.37	5.54	
H	OCH_3	CH_3	OAc	5.30	2.80	4.87
H	OAc	CH_3	OAc	6.30		4.83



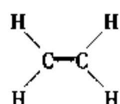
X	Y	δ_1	δ_2	δ_3	$\delta_{4\alpha}$	$\delta_{4\beta}$	δ_5	$J_{4\alpha4\beta}$	$J_{34\beta}$	$J_{34\alpha}$	J_{15}	$J_{14\alpha}$
OH	OH	5.88	5.88	4.66	1.51	2.66	4.66	−14.7	7.3	3.6	1.0	0.5
OBZ	OBZ	6.28	6.28	5.88	2.07	3.10	5.88	−15.0	7.5	4.0	0.8	
Br	Br	6.13	6.13	5.06	2.72	3.08	5.06	−16.5	6.5	1.8	1.0	



X	Y	δ_1	δ_2	δ_3	$\delta_{4\alpha}$	$\delta_{4\beta}$	δ_5	J_{15}
OH	OH	5.73	5.73	4.71	1.78	1.78	4.71	0.6
OBZ	OBZ	6.34	6.34	6.17	2.53	2.53	6.17	0.8

八、不同双键和三键体系的^{1}H-NMR 化学位移和偶合常数[66]

1. 乙烯



5.28

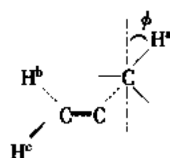
同碳偶合：$J_{gem}=2.5$

邻位偶合：$J_{cis}=11.6$

$J_{trans}=19.1$

R	J_{ab}	J_{ac}	J_{bc}
$-CH_3$	10.0	16.8	2.1
—F	4.7	12.7	−3.2
$-OCH_3$	7.0	14.1	−2.0
$-SCH_3$	10.3	16.4	−0.3
$-COCH_3$	10.7	18.7	1.3
—Li	19.3	23.9	7.1

2. 烯丙系

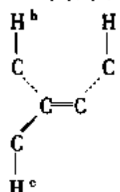


顺式：$J_{ab}=-3\sim+2$

反式：$J_{ac}=-3.5\sim+2.5$

ϕ	J_{ab}	J_{ac}
0°	−3.0	−3.5
90°	+1.8	+2.2
180°	−3.0	−3.5
270°	0	0.8

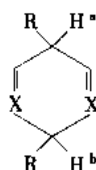
3. 高烯丙系



顺式：$|J|_{ab}=0\sim3$

反式：$|J|_{ac}=0\sim3$

一般：$J_{H-C-C-CH_3}\approx -J_{CH_3-C=C\ CH_3}$



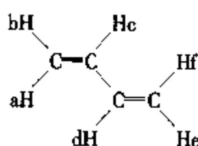
$J_{ab} = 5 \sim 11$



$J_{ab} = 0 \sim 7$

X = CH, N　　R 为任一取代基　　X = O, NH

4. 丁二烯

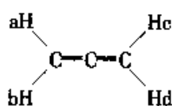


(a) 5.16
(b) 5.06
(c) 6.27

$J_{ab} = 1.8$
$J_{ac} = 17.1$
$J_{ad} = -0.8$
$J_{ae} = 0.6$
$J_{af} = 0.7$

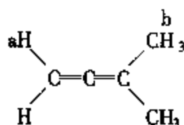
$J_{bc} = 10.2$
$J_{bd} = -0.9$
$J_{be} = 1.3$
$J_{cd} = 10.4$

5. 叠烯



4.67

$J_{ab} = -9$
$J_{ac} = -6$



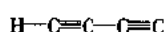
$|J|_{ab} = 3.0$

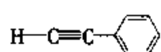
6. 炔衍生物

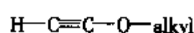

1.80


1.7 ~ 1.9


2.6 ~ 3.1

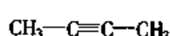

1.7 ~ 2.4


2.7 ~ 3.4


1.3

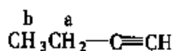

2.1 ~ 3.3

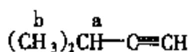

$|J| = 2.9$

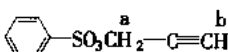

$|J| = 2.7$


$|J| = 2.2$


(a) 1.80
(b) 1.80


(a) 2.16
(b) 1.15


(a) 2.59
(b) 1.15


(a) ≈4.7
(b) 2.55


(a) 4.06
(b) 2.25

7. 不饱和脂环



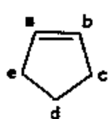
(a,b) 7.01
(c) 0.92

在衍生物中：$J_{ab} = 0.5 \sim 1.5$
$J_{bc} = 1.8$



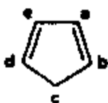
(a,b) 5.95
(c,d) 2.57

同碳偶合：$J_{cc'} = -12.0$
邻位偶合：$J_{ab} = 2.7$
$J_{bc} = -0.8$
$J_{cd}(cis) = 4.4$
$J_{cd}(trans) = 1.7$
远程偶合：$J_{ac} = 1.6$



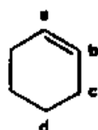
(a,b) 5.60
(c,e) 2.28
(d) 1.90

在衍生物中：$J_{ab} = 5.0 \sim 7.0$
$J_{bc} = 0.5$



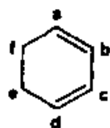
(a,e) 6.5
(b,d) 6.4
(c) 2.90

邻位偶合：$J_{ab} = 5.1$
$J_{bc} = 1.2$
远程偶合：$J_{ae} = 1.9$
$J_{ac} = -1.3$
$J_{ad} = 1.1$
$J_{bd} = 1.9$



(a,b) 5.59
(c) 1.96
(d) 1.65

在衍生物中：$J_{ab} = 8.5 \sim 11.0$
$J_{bc} = 1.5$



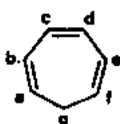
(a,d) 5.8
(b,c) 5.9
(e,f) 2.15

邻位偶合：$J_{ab} = 9.4$
$J_{bc} = 5.1$
远程偶合：$J_{ac} = 1.1$
$J_{ad} = 0.9$



(a,b) 5.71
(c) 2.11

在衍生物中：$J_{ab} = 9.0 \sim 12.5$
$J_{bc} = 3.7$



(a,f) 5.26
(b,e) 6.09
(c,d) 6.50
(g) 2.22

同碳偶合：$J_{gg'} = -13.0$
邻位偶合：$J_{ab} = 8.9$
$J_{bc} = 5.5$
$J_{cd} = 11.2$
$J_{ag} = 6.7$
远程偶合：$J_{ac} + J_{ad} = 1.5$
$J_{ae} = J_{af} = 0$
$J_{bd} = 0.8$
$J_{be} = -0.6$
$J_{bf} = 0$



(a,b) 5.56
(c) 2.11
(d,e) 1.5

在衍生物中：$J_{ab} = 10 \sim 13$
$J_{bc} = 5.3$

第五节 芳香烃及其衍生物的¹H-NMR 化学位移和偶合常数

一、取代苯衍生物的¹H-NMR 化学位移

表 4-26 取代基对苯环氢的化学位移的影响[66]

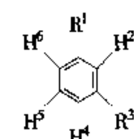
$\delta_H = 7.26 + Z_i$

取代基 X	Z_2	Z_3	Z_4	取代基 X	Z_2	Z_3	Z_4
—H	0	0	0	$—N^+(CH_3)_3I^-$	0.69	0.36	0.31
$—CH_3$	-0.20	-0.12	-0.22	$—NHCOCH_3$	0.12	-0.07	-0.28
$—CH_2CH_3$	-0.14	-0.06	-0.17	$—N(CH_3)COCH_3$	-0.16	0.05	-0.02
$—CH(CH_3)_2$	-0.13	-0.08	-0.18	$—NHNH_2$	-0.60	-0.08	-0.55
$—C(CH_3)_3$	0.02	-0.08	-0.21	—N═N—Ph	0.67	0.20	0.20
$—CH_2Cl$	0.00	0.00	0.00	—NO	0.58	0.31	0.37
$—CF_3$	0.32	0.14	0.20	$—NO_2$	0.95	0.26	0.38
$—CCl_3$	0.64	0.13	0.10	—SH	-0.08	-0.16	-0.22
$—CH_2OH$	-0.07	-0.07	-0.07	$—SCH_3$	-0.08	-0.10	-0.24
$—CH═CH_2$	0.06	-0.03	-0.10	—S—Ph	0.06	-0.09	-0.15
—CH═CH—Ph	0.15	-0.01	-0.16	$—SO_3CH_3$	0.60	0.26	0.33
—C≡CH	0.15	-0.02	-0.01	$—SO_2Cl$	0.76	0.35	0.45
—C≡C—Ph	0.19	0.02	0.00	—CHO	0.56	0.22	0.29
—Ph	0.37	0.20	0.10	$—COCH_3$	0.62	0.14	0.21
—F	-0.26	0.00	-0.20	$—COCH_2CH_3$	0.63	0.13	0.20
—Cl	0.03	-0.02	-0.09	$—COC(CH_3)_3$	0.44	0.05	0.05
—Br	0.18	-0.08	-0.04	—CO—Ph	0.47	0.13	0.22
—I	0.39	-0.21	0.00	—COOH	0.85	0.18	0.27
—OH	-0.56	-0.12	-0.45	$—COOCH_3$	0.71	0.11	0.21
$—OCH_3$	-0.48	-0.09	-0.44	$—COOCH(CH_3)_2$	0.70	0.09	0.19
$—OCH_2CH_3$	-0.46	-0.10	-0.43	—COO—Ph	0.90	0.17	0.27
—O—Ph	-0.29	-0.05	-0.23	$—CONH_2$	0.61	0.10	0.17
$—OCOCH_3$	-0.25	0.03	-0.13	—COCl	0.84	0.22	0.36
—OCO—Ph	-0.09	0.09	-0.08	—COBr	0.80	0.21	0.37
$—OSO_2CH_3$	-0.05	0.07	-0.01	—CH═N—Ph	≈0.6	≈0.2	≈0.2
$—NH_2$	-0.75	-0.25	-0.65	—CN	0.36	0.18	0.28
$—NHCH_3$	-0.80	-0.22	-0.68	$—Si(CH_3)_3$	0.22	-0.02	-0.02
$—N(CH_3)_2$	-0.66	-0.18	-0.67	$—PO(OCH_3)_2$	0.48	0.16	0.24

表 4-27 邻位双取代苯环氢的化学位移和偶合常数

X	Y	δ_3	δ_4	δ_5	δ_6	J_{34}	J_{45}	J_{56}	J_{35}	J_{46}	J_{36}
Cl	OCH_3	6.81	7.10	6.80	7.26	7.99	7.30	7.74	1.19	1.62	0.31
Br	OCH_3	6.87	7.15	6.73	7.44	8.31	7.63	7.80	1.54	1.63	0.19
I	OCH_3	6.71	7.20	6.61	7.69	8.05	7.17	7.55	1.38	1.62	0.29
OCH_3	OCH_3	6.75	6.75	6.75	6.75						
Cl	NO_2	7.82	7.41	7.49	7.54	8.23	7.13	7.67	1.17	1.41	0.78
Br	NO_2	7.78	7.44	7.40	7.71	7.86	7.53	8.27	1.66	1.22	0.19
I	NO_2	7.80	7.36	7.29	7.99	7.90	7.20	7.71	1.35	1.45	0.28
NO_2	NO_2	7.97	7.87	7.87	7.97						
Cl	CN	7.64	7.38	7.53	7.50	7.52	7.58	8.08	1.48	0.95	0.46
Br	CN	7.63	7.43	7.45	7.67	7.78	7.44	7.84	1.35	1.59	0.45
CN	CN	7.81	7.75	7.75	7.81						
NO_2	OCH_3	7.06	7.46	6.96	7.70	8.54	7.91	7.85	1.21	1.76	0.27
Cl	Cl	7.37	7.12	7.12	7.37						
Br	Br	7.55	7.19	7.19	7.55						
I	I	7.81	6.96	6.96	7.81						
Cl	Br	7.53	7.01	7.14	7.38						
Cl	I	7.79	6.84	7.21	7.37						
Br	I	7.78	6.88	7.16	7.55						

表 4-28 间位双取代苯环氢的化学位移



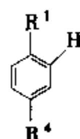
$\delta_i = 7.27 + Z_i$(取代基影响因素)

$2-H = A_{R^1} + A_{R^3}$　　$5-H = B_{R^1} + B_{R^3}$

$4-H = A_{R^3} + C_{R^1}$　　$6-H = A_{R^1} + C_{R^3}$

取代基 R	A	B	C	取代基 R	A	B	C
NH_2	-0.77	-0.27	-0.67	NO_2	+0.96	+0.16	+0.29
OMe	-0.48	-0.11	-0.41	CHO	+0.54	+0.20	+0.2
Me	-0.18	-0.11	-0.16	$COCH_3$	+0.64	+0.09	+0.1
Cl	0.00	-0.07	-0.16	COCl	+0.83	+0.16	+0.2
Br	+0.16	-0.13	-0.07	CN	+0.27	+0.10	+0.1
I	+0.36	-0.27	-0.07				

表 4-29 对位双取代苯环氢的化学位移



$\delta_i = 7.27 + Z_i$

R^4 \ R^1	NH_2	OMe	Me	Cl	Br	I	NO_2	CHO	$COCH_3$	COCl	CN
NH_2	-0.96	-0.66	-0.43	-0.27	-0.12	+0.07	+0.63	+0.21	+0.37	+0.56	0.00
OMe	-0.84	-0.55	-0.28	-0.11	+0.05	+0.24	+0.83	+0.41	+0.53	+0.72	+0.16
Me	-0.84	-0.55	-0.28	-0.11	+0.05	+0.24	+0.83	+0.41	+0.53	+0.72	+0.16
Cl	-0.81	-0.52	-0.24	-0.07	+0.09	+0.29	+0.88	+0.46	+0.58	+0.76	+0.20
Br	-0.86	-0.57	-0.30	-0.13	+0.02	+0.22	+0.79	+0.38	+0.51	+0.70	+0.14
I	-0.95	-0.65	-0.42	-0.27	-0.11	+0.07	+0.64	+0.22	+0.37	+0.56	0.00
NO_2	-0.66	-0.37	-0.04	+0.16	+0.32	+0.53	+1.14	+0.73	+0.80	+0.99	+0.43
CHO	-0.63	-0.35	-0.01	+0.20	+0.36	+0.58	+1.19	+0.77	+0.84	+1.03	+0.47
$COCH_3$	-0.70	-0.42	-0.10	+0.09	+0.25	+0.46	+1.06	+0.65	+0.73	+0.92	+0.36
COCl	-0.66	-0.37	-0.04	+0.16	+0.32	+0.53	+1.14	+0.73	+0.80	+0.99	+0.43
CN	-0.70	-0.41	-0.09	+0.10	+0.26	+0.47	+1.08	+0.66	+0.74	+0.93	+0.37

二、取代萘衍生物的¹H-NMR 化学位移和偶合常数

表 4-30 1,4-二取代萘的¹H-NMR 化学位移和偶合常数[48]

R^1	R^2	δ_2	δ_3	δ_5	δ_6	δ_7	δ_8	J_{23}	J_{56}	J_{57}	J_{58}	J_{67}	J_{68}	J_{78}	
OCH_3	OCH_3	6.70	6.70	8.19	7.45	7.45	8.19		8.3	1.4	0.3	6.6	1.4	8.3	
NO_2	NO_2	8.41	8.41	8.27	7.95	7.95	8.27		8.9	1.0	0.0	5.6	1.0	8.9	
Cl	Cl	7.39	7.39	8.23	7.57	7.57	8.23		8.3	1.5	0.3	6.3	1.5	8.3	
Cl	NH_2	7.29	6.57	7.71	7.41	7.52	8.11	8.0	8.4	0.7	0.6	6.9	1.2	8.6	$\delta_{NH_2} = 3.97$
Br	CH_3	7.44	7.01	7.85	7.45	7.59	8.22	7.8	8.6	1.1	1.1	7.5	2.0	8.0	$\delta_{CH_3} = 3.52$
NO_2	OCH_3	8.31	6.71	8.29	7.52	7.67	8.72	8.7	8.3	1.3	1.0	6.9	1.0	8.0	$\delta_{CH_3} = 4.00$
F	F	6.94	6.94	7.99	7.48	7.48	7.99		8.1	1.5	1.0	6.9	1.5	8.1	$J_{2,F} = 6.9$
															$J_{3,F} = 1.1$

表 4-31 1,4-二取代萘在不同溶剂中的^{1}H-NMR 化学位移[49]

X	环己烷			丙酮			乙腈		
	δ_2	δ_5	δ_6	δ_2	δ_5	δ_6	δ_2	δ_5	δ_6
CH_3	7.12	7.92	7.42	7.20	7.97	7.51	7.20	7.97	7.51
Cl	7.39	8.27	7.55	7.75	8.26	7.60	7.54	8.23	7.71
Br	7.56	8.24	7.56	7.77	8.29	7.77	7.69	8.20	7.72
OH	6.84	8.18	7.30						
NO_2	8.23	8.39	7.83	8.37	8.39	7.97	8.14	8.28	7.84

表 4-32 2,3-二取代萘的^{1}H-NMR 化学位移和偶合常数[48]

R^2	R^3	δ_1	δ_4	δ_5	δ_6	δ_7	δ_8	J_{14}	J_{56}	J_{57}	J_{58}	J_{67}	J_{68}	J_{78}
CH_3	CH_3	7.50	7.50	7.64	7.31	7.31	7.64		8.0	1.4	0.4	6.3	1.4	8.0 $\delta_{CH_3}=2.49$
Cl	Cl	7.87	7.87	7.65	7.43	7.43	7.65		8.0	1.8	0.5	7.7	1.8	7.7
Br	Br	8.07	8.07	7.45	7.45	7.45	7.65		7.9	1.7	0.5	7.7	1.7	7.7
NO_2	NO_2	7.88	7.88	8.32	7.90	7.90	8.32		8.3	1.2	0.0	6.2	1.2	8.3
Cl	Br	7.90	8.08	7.67	7.46	7.46	7.67	0.0	8.3	1.4	0.5	7.1	1.4	8.3
Cl	I	7.29	8.39	7.68	7.48	7.48	7.68	0.0	8.1	1.5	0.4	7.2	1.5	8.1

表 4-33 2,6-二取代萘的^{1}H-NMR 化学位移和偶合常数[48]

$R^2 = R^6$	δ_1	δ_3	δ_4	J_{13}	J_{14}	J_{34}	
$C(CH_3)_3$	7.73	7.52	7.75	1.7		8.7	$\delta_{CH_3}=1.41$
nC_6H_{13}	7.53	7.26	7.66	1.5		8.1	$\delta_{PhCH_2}=2.73$ $\delta_{CH_3}=0.88$ $J_{PhCH_2-CH_2}=7.2$
nC_8H_{17}	7.54	7.28	7.65	1.8		8.6	$\delta_{PhCH_2}=2.73$ $\delta_{CH_3}=0.87$ $J_{PhCH_2,CH_2}=7.3$
$nC_{10}H_{21}$	7.54	7.26	7.65	1.5		8.4	$\delta_{PhCH_2}=2.73$ $\delta_{CH_3}=0.88$ $J_{PhCH_2,CH_2}=7.1$
$nC_{12}H_{25}$	7.53	7.26	7.65	1.6		8.3	$\delta_{PhCH_2}=2.73$ $\delta_{CH_3}=0.88$ $J_{PhCH_2,CH_2}=6.9$
1,1,3,3-四甲基丁基	7.71	7.51	7.71	1.5		8.8	$\delta_{CH_2}=1.83$ $\delta_{CH_3}=0.74,1.45$
OCH_3	7.07	7.11	7.60	2.5	0.6	8.9	$\delta_{CH_3}=3.82$
COCl	8.80	8.36	8.12	1.3	0.3	8.6	
$COOCH_3$	8.58	8.08	7.94	1.5	0.3	8.6	$\delta_{CH_3}=3.97$

表 4-34 1,8-二取代萘的^{1}H-NMR 化学位移和偶合常数[48]

R^1	R^8	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	J_{23}	J_{24}	J_{34}	J_{56}	J_{57}	J_{67}
Cl	Cl	7.53	7.25	7.64	7.64	7.25	7.53	7.6	1.1	8.6	8.6	1.1	8.6
NO_2	NO_2	8.40	7.90	8.63	8.63	7.90	8.40	8.2	1.0	7.8	7.8	1.0	8.2
Cl	Br	7.59	7.22	7.75	7.61	7.31	7.88	7.1	1.1	8.6	7.8	1.2	7.5
Cl	NH_2	7.30	7.14	7.57	7.22	7.11	6.62	7.2	1.5	8.4	8.0	1.7	6.2 $\delta_{NH_2}=5.0$
Cl	NO_2	7.62	7.44	7.79	7.66	7.47	7.94	7.1	0.6	8.3	8.0	1.3	7.5

表 4-35 多取代萘衍生物的¹H-NMR 化学位移[50]

2,7-二叔丁基	H_1	H_3	H_4	H_5	H_6	H_8	*t*-Bu
无取代	7.82	7.50	7.76	7.76	7.50	7.82	
1-NO_2	—	7.68	7.95	7.98	7.68	7.37	1.32 1.43
4-NO_2	8.29	8.29		8.28	7.75	8.06	1.41 1.43
1,5-二-NO_2		8.07	8.44		8.54	7.65	1.44 1.49
4,5-二-NO_2	8.62	8.45			8.45	8.62	1.50
1,4,5-三-NO_2		8.77			8.78	7.71	1.45 1.54
1-NH_2		7.00	7.29	7.60	7.38	8.04	1.38 1.47
1-Cl		7.70	7.93	7.97	7.88	8.48	1.41 1.58
4-Cl	8.12	7.82		8.20	7.82	8.02	1.39
1,4-二-Cl		7.84		8.25	7.95	8.51	1.40 1.57
1,4,8-三-Cl		7.69		7.98	7.71		1.61
4-Br	7.97	7.97		8.07	7.70	7.90	1.39
1,4-二-Br		7.92		8.10	7.79	8.51	1.42 1.61
1,4-二-CO_2H		8.34		8.89	7.73	7.89	1.35 1.55
1-CN-4-CO_2H		8.25		8.87	7.88	8.25	1.44 1.66
1-CN-4-CO_2CH_3		8.25		8.74	7.90	8.25	1.45 1.65
4-SO_2NH_2	8.26	8.08		8.65	7.62	7.98	1.41
4-SO_3R	8.30	8.23		8.44	7.70	8.07	1.40 1.43
		7.43	7.43	7.43	7.43		1.42
	7.54	7.35			7.35	7.54	1.38
		7.80	8.28	8.28	7.80		1.56
		7.98	8.35	8.35	7.98		1.62
	8.5	8.02			8.02	8.55	1.47
		6.75		7.94	7.68	8.10	1.38
				8.15	7.97		1.37～1.48

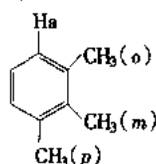
三、芳烃和脂芳烃衍生物的^{1}H-NMR化学位移和偶合常数[66]

(一) 不同芳环衍生物的^{1}H-NMR化学位移和偶合常数



7.26　　衍生物：$J_{ortho}=6.0\sim9.0$，$J_{meta}=1.0\sim3.0$，$J_{para}=0\sim1.0$

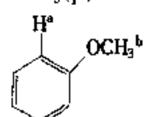
取代基氢的远程偶合：



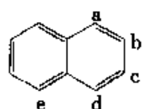
$J_{ao}=-0.6\sim-0.9$

$J_{am}=0\sim+0.3$

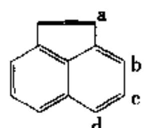
$J_{ap}\approx-0.6$



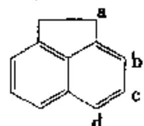
$J_{ab}=0\sim0.8$



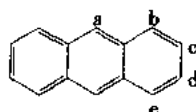
化学位移	偶合常数
(a) 7.66	$J_{ab}=8.5$(衍生物:8~9)
(b) 7.30	$J_{bc}=7.5$(衍生物:5~7)
	$J_{ac}=1.4$(衍生物:1~2)
	$J_{ad}=0.7$(衍生物:≈1)
	J_{ae}(衍生物):≈1



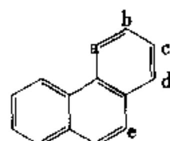
化学位移	偶合常数	偶合常数
(a) 7.15	$J_{ab}=0$	$J_{bc}=7$
(b) 7.90	$J_{ac}=0$	$J_{bd}=0.6$
(c) 7.58	$J_{ad}=0$	$J_{cd}=8$
(d) 7.79		



化学位移	偶合常数	偶合常数
(a) 3.34	$J_{bc}=6.7$	$J_{ab}=1.5$
(b) 7.11	$J_{cd}=8.1$	$J_{ad}=0.5$
(c) 7.31	$J_{bd}=1.2$	
(d) 7.46		

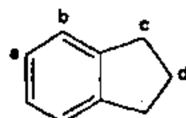


化学位移	偶合常数	偶合常数
(a) 8.31	$J_{bc}=8.4$	$J_{be}=0.5$
(b) 7.91	$J_{bd}=1.5$	$J_{cd}=6.0$
(c) 7.39		



化学位移	偶合常数	偶合常数
(a) 8.93	$J_{ab}=8.4$	$J_{bc}=7.2$
(b) 7.88	$J_{ac}=1.2$	$J_{bd}=1.3$
(c) 7.82	$J_{ad}=0.7$	$J_{cd}=8.1$
(d) 8.12		
(e) 7.71		

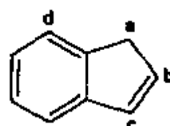
(二) 不同芳脂环衍生物的^{1}H-NMR化学位移和偶合常数



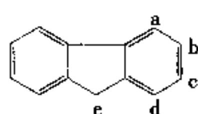
(a,b) ≈7.2

(c) 2.91

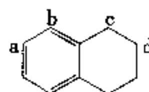
(d) 2.04



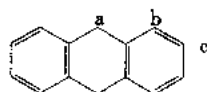
化学位移	偶合常数	偶合常数
(a) 3.33	$J_{ab}=2.0$	$J_{bc}=5.8$
(b) 6.50	$J_{ac}=2.0$	$J_{ad}=0.7$
(c) 6.82		



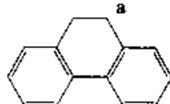
(a) 7.84　$J_{ab}=7.5$　$J_{bc}=6.5$
(b) 7.38　$J_{ac}=1.6$　$J_{bd}=1.6$
(c) 7.28　$J_{ad}=0.2$　$J_{cd}=7.2$
(d) 7.55
(e) 3.87



(a) 6.93
(b) 7.01
(c) 2.85
(d) 1.60

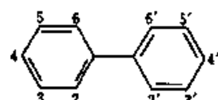


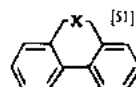
(a) 3.91
(b) 7.31
(c) 7.19



(a) 2.86

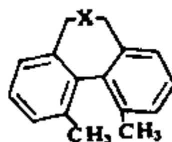
四、联苯衍生物的¹H-NMR 化学位移





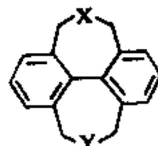
化　合　物	δ	J
联苯	7.4	
4,4′-二氟联苯	$\delta_2=7.37$	$J_{23}=8.7$
	$\delta_3=7.04$	
4,4′-二氯联苯	$\delta_2=\delta_3=7.38$	

X	δ(芳氢)	δ(次甲基)
O	7.47	4.34
NCH_3	4.76	3.35
C═O	7.38	3.52
S	7.32	3.35,3.44(二宽峰)



X	δ(芳氢)	δ(次甲基)	δ(甲基)	J_{AB}
O	7.29	4.00,4.39	2.20	11.0
NCH_3	7.22	3.02,3.35	2.19	12.1
CH_2	7.20	1.67,2.58	2.14	多峰

X	δ(芳氢)	δ(次甲基)	δ(甲基)	J_{AB}
C═O	7.23	3.32,3.53	2.20	15.2
	7.19	3.25	2.08	

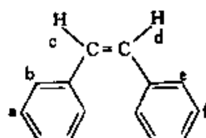


X	Y	δ(芳氢)	δ(次甲基)	J_{AB}
O	O	7.52	4.18,4.55	11.5
NCH_3	NCH_3	7.38	3.21,3.54	12.5
C═O	C═O	7.30	3.57(多峰)	
CH_2	CH_2	7.20	1.9～2.8(多峰)	

X	Y	δ(芳氢)	δ(次甲基)	J_{AB}
S	S	7.29	3.29,3.38	12.7
O	S	7.38	4.10,4.47	11.5
			3.34,3.53	12.7

五、二苯乙烯衍生物的^{1}H-NMR化学位移和偶合常数

表 4-36　顺-1,2-二苯乙烯衍生物的^{1}H-NMR化学位移和偶合常数[52]

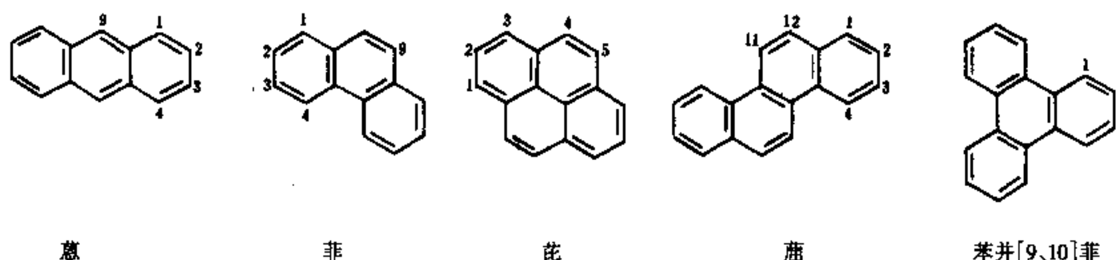


取代基	δ_a	δ_b	δ_c	δ_d	J_{ab}	J_{ba}	J_{cd}	J_{dc}	δ_e	δ_f	J_{ef}	J_{fe}
4-OCH_3	6.76	7.19	6.50	6.50	8.9	8.9						
3-NH_2				6.53			12.4	≈12.3				
4-F	6.84	6.93	6.56		8.8	8.7	≈12.5	≈12.5				
3-OCH_3				6.59			12.5	12.5				
4-Cl			6.52	6.62			12.3	12.3				
3-Cl			6.52	6.65			12.3	12.3				
4-CN	7.49	7.33	6.57	6.77	8.4	8.5	12.3	12.3				
4-NO_2	8.06	7.36	6.60	6.81	8.7	9.2	12.1	12.2				
4-$N(CH_3)_2$ 4'-NO_2	6.56	7.11	6.62	6.42	9.0	9.1	12.2	12.2	7.45	8.08	8.9	9.0
4-OCH_3,4'-NO_2	6.78	7.14	6.63	6.51	8.8	9.0	12.3	12.2	7.39	8.08	9.0	8.9
4-Cl,4'-NO_2	7.12	7.22	6.74	6.64	8.8	8.7	12.2	12.5	7.35	8.09	8.9	8.8

表 4-37　反-1,2-二苯乙烯衍生物的^{1}H-NMR化学位移和偶合常数[53]

取代基	δ_a	δ_b	δ_c	δ_d	J_{ab}	J_{ba}	J_{cd}	J_{dc}
4-$N(CH_3)_2$	6.71	7.41	7.04	6.91	8.9	8.9	16.5	16.5
4-NH_2	6.67	7.36	7.02	6.92	8.6	8.6	16.4	16.4
4-OH	6.81	7.40	7.04	6.97	8.7	8.6	16.5	16.5
4-OCH_3	6.89	7.43	7.06	6.98	8.7	8.7	16.5	16.5
4-Cl			7.07				16.7	16.7
4-F			7.07				16.6	16.6
4-Br	7.36	7.48	7.04	7.08	8.7	8.7	16.5	16.5
4-CN			7.09	7.22			16.5	16.5
4-NO_2	8.23	7.63	7.15	7.28	8.9	8.9	16.5	16.5
4-$N(CH_3)_2$,4'-NO_2	6.71	7.44	7.20		8.8	8.7	≈16.0	
4-NH_2,4'-NO_2	6.69	7.38	7.18		8.4	8.5	16.2	
4-OH,4'-NO_2	6.85	7.42	7.21		8.9	8.9	16.1	
4-OCH_3,4'-NO_2	6.93	7.49	7.22		8.6	8.6	16.2	
4-Cl,4'-NO_2	7.38	7.46	7.22		8.7	8.7	16.1	
4-NO_2,4'-NO_2	8.25	7.67	7.30					

六、稠环芳烃化合物的¹H-NMR化学位移和偶合常数



蒽　　菲　　芘　　䓛　　苯并[9、10]菲

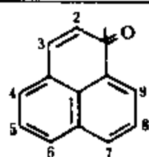
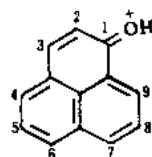
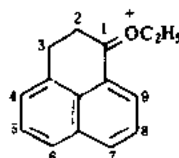
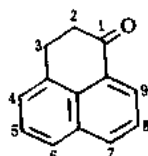
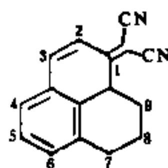
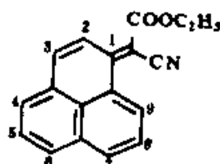
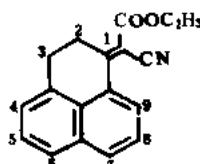
表 4-38　稠环芳烃的¹H-NMR化学位移和偶合常数(一)[54,55]

化合物	δ_1	δ_2	δ_3	δ_4	δ_9	$\delta_{其他}$	J
蒽	7.91	7.39			8.31		$J_{12}=8.3$; $J_{23}=6.5$
菲	8.12	7.82	7.88	8.93	7.71		$J_{12}=8.0\sim9.0$; $J_{23}=6.9\sim7.3$;
芘		7.99	8.16	8.06			$J_{34}=8.0\sim8.5$; $J_{13}=0.9\sim1.6$;
䓛	7.5~7.9	7.5~7.9	7.5~7.9	8.7		δ_{11} 8.65	$J_{24}=1.2\sim1.8$; $J_{14}=0.3\sim0.7$;
苯并[9、10]菲	8.56	7.61				δ_{12} 7.95	$J_{12}=8\sim8.4$; $J_{45}=9.2\sim9.5$

表 4-39　稠环芳烃的¹H-NMR化学位移和偶合常数(二)

化合物	数据
	$\delta_{1\text{-H}}=3.91$; $\delta_{2\text{-H}}=5.88$; $\delta_{3\text{-H}}=6.49$; $\delta_{4\text{-H}}=7.08$; $\delta_{5\text{-H}}=7.23$; $\delta_{6\text{-H}}=7.45$; $\delta_{7\text{-H}}=7.42$; $\delta_{8\text{-H}}=7.16$; $\delta_{9\text{-H}}=6.87$; $\delta_{1\text{-H}}=3.88$; $\delta_{2\text{-H}}=5.83$; $\delta_{3\text{-H}}=6.43$; $\delta_{4\text{-H}}=7.02$; $\delta_{5\text{-H}}=7.17$; $\delta_{6\text{-H}}=7.39$; $\delta_{7\text{-H}}=7.36$; $\delta_{8\text{-H}}=7.09$; $\delta_{9\text{-H}}=6.80$; $\delta_{1\text{-H}}=3.65$; $\delta_{2\text{-H}}=5.66$; $\delta_{3\text{-H}}=6.41$; $\delta_{4\text{-H}}=6.88$; $\delta_{5\text{-H}}=7.13$; $\delta_{6\text{-H}}=7.38$; $\delta_{7\text{-H}}=7.35$; $\delta_{8\text{-H}}=7.07$; $\delta_{9\text{-H}}=6.77$ $J_{12}=4.0$; $J_{13}=2.1$; $J_{14}=1.6$; $J_{16}=1.1$; $J_{17}=0.7$; $J_{19}=1.2$; $J_{23}=9.6$; $J_{45}=7.0$; $J_{46}=1.6$; $J_{56}=7.8$; $J_{78}=8.2$; $J_{79}=1.3$; $J_{89}=6.8$
SbCl₆	$\delta_{1\text{-H}}=\delta_{3\text{-H}}=\delta_{4\text{-H}}=\delta_{6\text{-H}}=\delta_{7\text{-H}}=\delta_{9\text{-H}}=9.30$; $\delta_{2\text{-H}}=\delta_{5\text{-H}}=\delta_{8\text{-H}}=8.48$ $J_{邻}=7.2$
L⁺	$\delta_{1\text{-H}}=\delta_{3\text{-H}}=\delta_{4\text{-H}}=\delta_{6\text{-H}}=\delta_{7\text{-H}}=\delta_{9\text{-H}}=5.17$; $\delta_{2\text{-H}}=\delta_{5\text{-H}}=\delta_{8\text{-H}}=5.91$ $J_{邻}=7.5$
	$\delta_{1\text{-H}}=\delta_{3\text{-H}}=3.01$; $\delta_{2\text{-H}}=1.97$; $\delta_{4\text{-H}}=\delta_{9\text{-H}}=7.12$; $\delta_{5\text{-H}}=\delta_{8\text{-H}}=7.28$; $\delta_{6\text{-H}}=\delta_{7\text{-H}}=7.59$ $\delta_{1\text{-H}}=\delta_{3\text{-H}}=2.76$; $\delta_{2\text{-H}}=1.70$; $\delta_{4\text{-H}}=\delta_{9\text{-H}}=7.00$; $\delta_{5\text{-H}}=\delta_{8\text{-H}}=7.20$; $\delta_{7\text{-H}}=7.53$ $J_{19}\approx1.0$; $J_{17}\approx0.7$; $J_{45}=6.8$; $J_{46}=1.4$; $J_{56}=8.0$

续表

	$\delta_{2\text{-H}}=6.66$; $\delta_{3\text{-H}}=7.63$; $\delta_{4\text{-H}}=7.63$; $\delta_{5\text{-H}}=7.48$; $\delta_{6\text{-H}}=7.91$; $\delta_{7\text{-H}}=8.08$; $\delta_{8\text{-H}}=7.67$; $\delta_{9\text{-H}}=8.52$ $\delta_{2\text{-H}}=6.63$; $\delta_{3\text{-H}}=7.06$; $\delta_{4\text{-H}}\approx7.1$; $\delta_{5\text{-H}}=7.05$; $\delta_{6\text{-H}}=7.43$; $\delta_{7\text{-H}}=7.55$; $\delta_{8\text{-H}}=7.19$; $\delta_{9\text{-H}}=8.62$ $J_{23}=9.6$; $J_{45}=7.5$; $J_{78}=8.0$; $J_{89}=7.2$
	$\delta_{2\text{-H}}=7.76$; $\delta_{3\text{-H}}=8.88$; $\delta_{4\text{-H}}=8.78$; $\delta_{5\text{-H}}=8.20$; $\delta_{6\text{-H}}=8.86$; $\delta_{7\text{-H}}=9.01$; $\delta_{8\text{-H}}=8.30$; $\delta_{9\text{-H}}=9.46$ $J_{23}=9.0$; $J_{45}=7.6$; $J_{46}=1.4$; $J_{56}=7.6$; $J_{78}=7.8$; $J_{89}=7.7$
	$\delta_{2\text{-H}}=7.81$; $\delta_{3\text{-H}}=9.04$; $\delta_{4\text{-H}}=\delta_{6\text{-H}}=8.57\sim8.60$; $\delta_{5\text{-H}}=8.14$; $\delta_{7\text{-H}}=8.96$; $\delta_{8\text{-H}}=8.21$; $\delta_{9\text{-H}}=9.26$ ($\delta_{CH_2}=4.96$; $\delta_{CH_3}=1.78$) $\delta_{2\text{-H}}=7.88$; $\delta_{3\text{-H}}=9.15$; $\delta_{4\text{-H}}=\delta_{6\text{-H}}=8.90\sim8.95$; $\delta_{5\text{-H}}=8.24$; $\delta_{7\text{-H}}=9.07$; $\delta_{8\text{-H}}=8.34$; $\delta_{9\text{-H}}=9.15$ ($\delta_{CH_2}=4.99$; $\delta_{CH_3}=1.84$) $J_{23}=9.2$; $J_{45}=7.7$; $J_{46}=1.3$; $J_{56}=7.7$; $J_{78}=7.8$; $J_{79}=1.2$; $J_{89}=7.8$ $J_{23}=9.3$; $J_{45}=7.5$; $J_{46}=1.2$; $J_{56}=7.5$; $J_{78}=7.8$; $J_{79}=1.2$; $J_{89}=7.9$
	$\delta_{2\text{-H}}=2.81$; $\delta_{3\text{-H}}=3.22$; $\delta_{4\text{-H}}=7.25$; $\delta_{5\text{-H}}=7.32$; $\delta_{6\text{-H}}=7.62$; $\delta_{7\text{-H}}=7.90$; $\delta_{8\text{-H}}=7.41$; $\delta_{9\text{-H}}=8.08$ $\delta_{2\text{-H}}=2.57$; $\delta_{3\text{-H}}=2.84$; $\delta_{4\text{-H}}=6.98$; $\delta_{5\text{-H}}=7.17$; $\delta_{6\text{-H}}=7.46$; $\delta_{7\text{-H}}=7.66$; $\delta_{8\text{-H}}=7.20$; $\delta_{9\text{-H}}=8.22$ $\delta_{2\text{-H}}=2.77$; $\delta_{3\text{-H}}=3.07$; $\delta_{4\text{-H}}=7.20$; $\delta_{5\text{-H}}=7.29$; $\delta_{6\text{-H}}=7.51$; $\delta_{7\text{-H}}=7.85$; $\delta_{8\text{-H}}=7.29$; $\delta_{9\text{-H}}=7.93$ $J_{78}=8.2$; $J_{79}=1.3$; $J_{89}=7.1$ $J_{34}=1.2$; $J_{36}=0.9$; $J_{45}=6.9$; $J_{56}=7.9$; $J_{78}=8.0$; $J_{79}=1.3$; $J_{89}=7.1$ $J_{34}\approx1.0$; $J_{36}\approx0.6$; $J_{78}=8.3$; $J_{79}=1.1$; $J_{89}=7.4$
	$\delta_{2\text{-H}}=7.50$; $\delta_{3\text{-H}}=7.50$; $\delta_{4\text{-H}}=7.77$; $\delta_{5\text{-H}}=7.64$; $\delta_{6\text{-H}}=8.02$; $\delta_{7\text{-H}}=8.23$; $\delta_{8\text{-H}}=7.78$; $\delta_{9\text{-H}}=9.39$ $\delta_{2\text{-H}}=7.36$; $\delta_{3\text{-H}}=7.65$; $\delta_{4\text{-H}}=7.90$; $\delta_{5\text{-H}}=7.74$; $\delta_{6\text{-H}}=8.13$; $\delta_{7\text{-H}}=8.32$; $\delta_{8\text{-H}}=7.78$; $\delta_{9\text{-H}}=9.23$; $J_{45}=7.0$; $J_{46}=1.5$; $J_{78}=8.0$; $J_{79}=1.0$; $J_{89}=7.8$ $J_{23}=9.6$; $J_{45}=7.3$; $J_{46}=1.3$; $J_{56}=7.8$; $J_{78}=8.0$ $J_{79}<1$; $J_{89}=8.0$
	$\delta_{2\text{-H}}=8.46$; $\delta_{3\text{-H}}=7.30$; $\delta_{4\text{-H}}=7.59$; $\delta_{5\text{-H}}=7.52$; $\delta_{6\text{-H}}=7.88$; $\delta_{7\text{-H}}=8.06$; $\delta_{8\text{-H}}=7.67$; $\delta_{9\text{-H}}=9.35$ $\delta_{2\text{-H}}=8.26$; $\delta_{3\text{-H}}=7.47$; $\delta_{6\text{-H}}=7.98$; $\delta_{7\text{-H}}=8.16$; $\delta_{8\text{-H}}\approx7.7$; $\delta_{9\text{-H}}=9.11$ $J_{23}=10.0$; $J_{45}=7.0$; $J_{46}=1.0$; $J_{56}=8.0$; $J_{78}=8.0$; $J_{79}\approx1$; $J_{89}=7.8$ $J_{23}=9.6$; $J_{89}=8.0$
	$\delta_{2\text{-H}}=3.47$; $\delta_{3\text{-H}}=3.20$; $\delta_{4\text{-H}}=7.28$; $\delta_{5\text{-H}}=7.38$; $\delta_{6\text{-H}}=7.68$; $\delta_{7\text{-H}}=7.92$; $\delta_{8\text{-H}}=7.47$; $\delta_{9\text{-H}}=8.20$ $\delta_{2\text{-H}}=3.50$; $\delta_{3\text{-H}}=3.31$; $\delta_{4\text{-H}}=7.34$; $\delta_{5\text{-H}}=7.43$; $\delta_{6\text{-H}}=7.72$ $\delta_{7\text{-H}}=8.01$; $\delta_{8\text{-H}}=7.50$; $\delta_{9\text{-H}}=8.17$ $J_{34}\approx1.0$; $J_{36}<1.0$; $J_{45}=7.3$; $J_{46}=1.2$; $J_{56}=8.1$; $J_{78}=8.2$; $J_{79}=1.2$; $J_{89}=7.4$ $J_{34}\approx1.0$; $J_{36}<1.0$; $J_{45}=7.0$; $J_{56}=8.0$; $J_{78}=8.2$; $J_{79}=1.0$; $J_{89}=7.3$

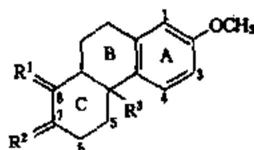
续表

结构	数据
C_2H_5O, $COOC_2H$, CN	$\delta_{2\text{-H}}=8.22$; $\delta_{4\text{-H}}=8.14$; $\delta_{5\text{-H}}=7.55$; $\delta_{6\text{-H}}=7.94$; $\delta_{7\text{-H}}=8.02$; $\delta_{8\text{-H}}=7.62$; $\delta_{9\text{-H}}=9.40$ $J_{45}=7.4$; $J_{46}=1.0$; $J_{56}=8.0$; $J_{78}=8.0$; $J_{79}<1$; $J_{89}=7.8$
$C_2O_3H^+$, $COOC_2H_5$, CN	$\delta_{2\text{-H}}=8.12$; $\delta_{4\text{-H}}=9.00$; $\delta_{5\text{-H}}=8.27$; $\delta_{6\text{-H}}=9.19$; $\delta_{7\text{-H}}=9.11$; $\delta_{8\text{-H}}=8.34$; $\delta_{9\text{-H}}=9.53$ $J_{45}=8.0$; $J_{46}\approx1.0$; $J_{56}=8.0$; $J_{79}=1.2$; $J_{89}=8.0$
Br, $COOC_2H$, CN	$\delta_{2\text{-H}}=8.95$; $\delta_{4\text{-H}}=8.06$; $\delta_{5\text{-H}}=7.57$; $\delta_{6\text{-H}}=7.92$; $\delta_{7\text{-H}}=8.06$; $\delta_{8\text{-H}}=7.67$; $\delta_{9\text{-H}}=9.30$ $\delta_{2\text{-H}}=8.66$; $\delta_{4\text{-H}}=8.1$; $\delta_{5\text{-H}}=7.58$; $\delta_{6\text{-H}}=7.95$; $\delta_{7\text{-H}}=8.10$; $\delta_{8\text{-H}}=7.62$; $\delta_{9\text{-H}}=9.05$ $J_{45}=7.2$; $J_{46}\approx1.0$; $J_{56}=8.0$; $J_{78}=7.8$; $J_{79}=1.0$; $J_{89}=7.8$ $J_{45}\approx7.5$; $J_{56}=8.0$; $J_{78}\approx8.0$; $J_{89}=7.8$
NOH	$\delta_{2\text{-H}}=7.09$; $\delta_{3\text{-H}}=7.36$; $\delta_{4\text{-H}}\approx7.4$; $\delta_{5\text{-H}}\approx7.35$; $\delta_{6\text{-H}}=7.70$; $\delta_{7\text{-H}}=7.82$; $\delta_{8\text{-H}}=7.51$; $\delta_{9\text{-H}}=8.32$ $\delta_{2\text{-H}}=7.67$; $\delta_{3\text{-H}}=8.18$; $\delta_{4\text{-H}}=8.15$; $\delta_{5\text{-H}}=7.86$; $\delta_{6\text{-H}}=8.32$; $\delta_{7\text{-H}}=8.53$; $\delta_{8\text{-H}}=7.96$; $\delta_{9\text{-H}}=8.71$ $J_{23}=10.0$; $J_{78}=8.0$; $J_{79}=1.0$; $J_{89}=7.5$ $J_{23}=9.5$; $J_{45}=7.2$; $J_{46}=1.0$; $J_{56}\approx8.1$; $J_{78}=7.6$; $J_{79}=0.7$; $J_{89}=7.6$
N-	$\delta_{2\text{-H}}=6.63$; $\delta_{3\text{-H}}=7.09$; $\delta_{4\text{-H}}=7.35$; $\delta_{5\text{-H}}\approx7.35$; $\delta_{6\text{-H}}=7.75$; $\delta_{7\text{-H}}=7.91$; $\delta_{8\text{-H}}=7.60$; $\delta_{9\text{-H}}=8.72$; $\delta_{2\text{-H}}=7.41$; $\delta_{3\text{-H}}=8.34$; $\delta_{4\text{-H}}=8.35$; $\delta_{5\text{-H}}=7.98$; $\delta_{6\text{-H}}=8.53$; $\delta_{7\text{-H}}=8.76$; $\delta_{8\text{-H}}=8.18$; $\delta_{9\text{-H}}=9.19$ $J_{23}=10.0$; $J_{78}=8.0$; $J_{89}\approx1.3$; $J_{89}=7.3$ $J_{23}=9.5$; $J_{45}\approx8.1$; $J_{46}=1.0$; $J_{56}=7.4$; $J_{78}=8.0$; $J_{79}=1.0$; $J_{89}\approx7.8$

七、其他芳烃化合物的^{1}H-NMR 化学位移和偶合常数

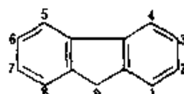
表 4-40　部分还原多环芳烃的^{1}H-NMR 化学位移数据[56]

R	δ_1	δ_3	δ_4	δ_{OCH_3}	δ_{CH_3}	R	δ_1	δ_3	δ_4	δ_{OCH_3}	δ_{CH_3}
H	6.57	6.63	6.96	3.73		C_2H_5	6.62	6.70	7.11	3.76	0.95
CH_3	6.62	6.72	7.12	3.76	1.26	$CH(CH_3)_2$	6.61	6.69	7.13	3.77	0.93,0.82



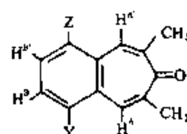
R^1	R^2	R^3	B/C	δ_1	δ_3	δ_4	δ_{OCH_3}	$\delta_{其他质子}$
H_2	O	H	*trans*	6.63	6.72	7.23	3.77	
O	H_2	H	*trans*	6.64	6.73	7.22	3.77	
$(CH_3)_2$	H_2	CH_3	*trans*	6.58	6.68	7.16	3.74	4bCH_3 1.20
								8CH_3 1.04,0.92
H_2	O	H	*cis*	6.64	6.73	7.12	3.76	
O	H_2	H	*cis*	6.62	6.71	7.06	3.76	
$(CH_3)_2$	H_2	CH_3	*cis*	6.56	6.65	7.14	3.74	4bCH_3 1.13
								8βCH_3 0.92
								8αCH_3 0.38

表 4-41 芴衍生物的¹H-NMR 化学位移和偶合常数[48]



R^2	R^4	R^5	R^7	R^8	δ_1	δ_2	δ_3	δ_4	$\delta_{其他}$	J
H	H	H	H	H	7.55	7.28	7.38	7.84	$\delta_{CH_3}=3.87$	$J_{12}=7.17$
										$J_{13}=1.64$
										$J_{14}=0.19$
										$J_{23}=6.51$
										$J_{24}=1.56$
										$J_{34}=7.52$
NH_2	H	H	H	H	7.01		6.84	7.42	$\delta_{NH_2}=5.5$	$J_{13}=2.17$
										$J_{14}=0.21$
										$J_{34}=7.99$
NO_2	H	H	H	H	8.41		8.17	7.98		$J_{12}=1.89$
										$J_{14}=0.0$
										$J_{34}=7.93$
NH_2	H	H	NH_2	H	6.87		6.72	7.18	$\delta_{NH_2}=5.04$	$J_{13}=2.09$
										$J_{14}=0.13$
										$J_{34}=7.94$
NH_2	H	H	H	NO_2	6.88		6.80	7.49	$\delta_5=7.59$	$J_{13}=2.00$
									$\delta_6=8.28$	$J_{14}=0.03$
									$\delta_8=7.98$	$J_{34}=7.89$
									$\delta_{NH_2}=4.3$	$J_{56}=7.52$
										$J_{58}=0.00$
										$J_{68}=1.71$
NO_2	NO_2	H	NO_2	H	8.58		8.99		$\delta_5=8.14$	$J_{13}=2.08$
									$\delta_6=8.56$	$J_{56}=8.60$
									$\delta_8=8.39$	$J_{58}=0.37$
										$J_{68}=2.24$
NO_2	NO_2	NO_2	NO_2	H	8.75		8.94			$J_{13}=2.05$

表 4-42 环庚(*f*)茚衍生物的^{1}H-NMR 化学位移数据[57]



Y	Z	H^{B1}及 H^B ($CDCl_3$)	H^A 及 H^{A1} ($CDCl_3$)	H^{A1}及 H^A (F_3CCO_2H)	H^{B1}及 H^B (F_3CCO_2H)
H	H	7.20	7.20	9.35	8.30～8.80
H	NH_2	6.85～7.50	7.67,7.83	—	—
H	NHAc	—	—	8.98,9.11	8.05～8.45
H	OCH_3	6.60～7.15	7.22,7.95	—	—
H	Br	7.00～7.65	7.15,7.86	9.00,9.57	7.80～8.55
H	OH	—	—	9.22,10.10	7.75～8.50
NO_2	NHAc	—	—	7.80～8.30	7.80～8.30
NO_2	NH_2	—	—	8.00～8.30	8.00～8.30
Br	Br	—	—	8.62	7.71
H	NAc_2	7.30～7.80	7.30～7.80	8.35,8.52	7.85～8.35
H	NO_2	—	—	7.80～8.40	7.80～8.40
H	NH_3^+	—	—	7.80～8.40	7.80～8.40

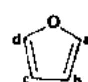
表 4-43 富烯衍生物的^{1}H-NMR 化学位移数据[58]

化合物	$\delta_{CH_3(CH_2)}$	$\delta_{环氢}$①	δ_{Ph}②	化合物	$\delta_{CH_3(CH_2)}$	$\delta_{环氢}$①	δ_{Ph}②
富烯(Fulvene)	5.78	6.11,6.44		二苄富烯	3.66	6.52	7.15
二甲富烯	2.13	6.30		二苯富烯		6.30	7.28

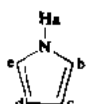
① 除富烯外,信号均取之裂分峰的中心。
② 信号取之发生裂分的最强峰。

第六节 五元芳杂环化合物的^{1}H-NMR 化学位移和偶合常数

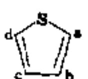
一、一般五元芳杂环化合物的^{1}H-NMR 化学位移和偶合常数



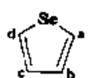
(a,d) 7.38　$J_{ab}=1.8$　$J_{ad}=1.5$
(b,c) 6.30　$J_{ac}=0.9$　$J_{bc}=3.4$



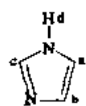
(a) 7～12　$J_{ab}=2.6$　$J_{bd}=1.3$
(b,e) 6.62　$J_{ac}=2.3$　$J_{be}=2.1$
(c,d) 6.05　$J_{bc}=2.6$　$J_{cd}=3.5$



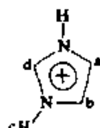
(a,d) 7.20　$J_{ab}=4.8$　$J_{ad}=2.8$
(b,c) 6.96　$J_{ac}=1.0$　$J_{bc}=3.5$



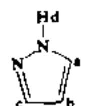
(a,d) 7.70　$J_{ab}=5.4$　$J_{ad}=2.5$
(b,c) 7.12　$J_{ac}=1.1$　$J_{bc}=3.6$



(a,b) 7.13 $J_{ab}=1\sim2$
(c) 7.70 $J_{ac}=1\sim2$
(d) 13.4 $J_{bc}=0.5\sim1.5$

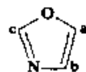


(a,b) 7.6 $J_{ac}+J_{bc}=4.4$
(c) 12 $J_{cd}=2.4$
(d) 8.6 $J_{ad}=1.4$

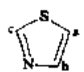


(a,c) 7.55 $J_{ab}=2.1$
(b) 6.25
(d) 13.7

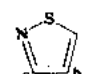
$J_{ab}=2\sim3$
$J_{bc}=1\sim2$
$J_{ac}=0.5\sim1$



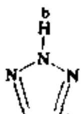
(a) 7.69 $J_{ab}=0.8$
(b) 7.09 $J_{ac}=0.5$
(c) 7.95



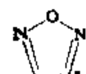
(a) 7.41 $J_{ab}=3.2$
(b) 7.98 $J_{ac}=1.9$
(c) 8.88 $J_{bc}=0$



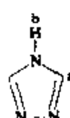
(a) 8.72 $J_{ab}=4.7$
(b) 7.26 $J_{ac}<0.4$
(c) 8.56 $J_{bc}=1.7$



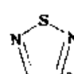
(a) 7.75
(b) 12



(a) 8.19



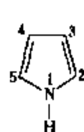
(a) 8.27
(b) 13.5



(a) 8.58

二、吡咯衍生物的^{1}H-NMR 化学位移

吡咯衍生物^{1}H-NMR 化学位移的计算如下[48,59,60]：



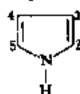
$\delta_{H_1}=7\sim12$
$\delta_{H_2}=6.62+Z_{i2}$
$\delta_{H_3}=6.05+Z_{i3}$
$\delta_{H_4}=6.05+Z_{i4}$
$\delta_{H_5}=6.62+Z_{i5}$

1-取代基 ($i=1$)	$Z_{12}=Z_{15}$	$Z_{13}=Z_{14}$	1-取代基 ($i=1$)	$Z_{12}=Z_{15}$	$Z_{13}=Z_{14}$
—H	0	0	—CH_2-ph	-0.12	-0.04
—CH_3	-0.25	-0.13	—ph	0.33	0.14
—CH_2CH_3	-0.16	-0.12	—$COCH_3$	0.56	0.12

2-或 5-取代基 ($i=2$或5)	$Z_{23}=Z_{54}$	$Z_{24}=Z_{53}$	$Z_{25}=Z_{52}$	2-或 5-取代基 ($i=2$或5)	$Z_{23}=Z_{54}$	$Z_{24}=Z_{53}$	$Z_{25}=Z_{52}$
—H	0	0	0	—CHO	0.93	0.27	0.61
—CH_3	-0.33	-0.16	-0.26	—$COCH_3$	0.78	0.10	0.44
—NO_2	1.06	0.24	0.43	—$COOCH_3$	0.79	0.13	0.29
—SCH_3	0.18	0.05	0.10	—CN	0.83	0.23	0.51
—SCN	0.48	0.10	0.28				

3-或 4-取代基 ($i=3$或4)	$Z_{32}=Z_{45}$	$Z_{34}=Z_{43}$	$Z_{35}=Z_{42}$	3-或 4-取代基 ($i=3$或4)	$Z_{32}=Z_{45}$	$Z_{34}=Z_{43}$	$Z_{35}=Z_{42}$
—H	0	0	0	—$COCH_3$	0.79	0.63	0.15
—CH_3	-0.34	-0.20	-0.20	—$COOCH_3$	0.90	0.73	0.16
—NO_2	1.04	0.70	0.13				

表 4-44 部分吡咯衍生物的^{1}H-NMR 化学位移和偶合常数



R^2	R^3	R^4	R^5	δ_2	δ_3	δ_4	δ_5	$\delta_{其他}$	J
H	H	H	H	6.68	6.12			$\delta_{NH}=9.25$	$J_{23}=2.6$; $J_{24}=1.3$; $J_{25}=2.1$; $J_{34}=3.7$; $J_{2NH}=2.6$; $J_{3NH}=2.3$
									J_{34}　J_{35}　J_{45}
CH_3	H	H	H		5.75	5.96	6.52	$\delta_{CH_3}=2.24$	3.40　1.50　2.45
CN	H	H	H		6.88	6.28	7.13		3.74　1.45　2.62 (其他: $J_{3NH}=2.25$; $J_{4NH}=2.42$; $J_{5NH}=2.70$)
CHO	H	H	H		6.93	6.26	7.13	$\delta_{CHO}=9.47$	3.80　1.40　2.40 (其他: $J_{4NH}=2.4$; $J_{5NH}=1.15$)
$COCH_3$	H	H	H		6.90	6.19	7.02		3.75　1.35　2.40 (其他: $J_{3NH}=2.50$; $J_{4NH}=2.4$; $J_{5NH}=3.00$)
COOH	H	H	H		6.78	6.07	6.61		3.6　1.6　2.5
H	$COOCH_3$	H	H	7.44		6.57	6.76		$J_{24}=1.40$; $J_{25}=1.95$; $J_{45}=2.80$
CH_3	CH_3	H	H			0.62	1.17	$\delta_{NH}=3.08$; $\delta_{CH_3}=-3.25$, -3.30	$J_{45}=J_{4NH}=J_{5NH}=2.6$
CH_3	$COOCH_3$	H	H			6.44	6.50		$J_{45}=3.10$
CH_3	H	CH_3	H		0.62		1.05	$\delta_{NH}=1.65$; $\delta_{CH_3}=-3.02$, -3.15	
CH_3	H	H	CH_3		0.62	0.62		$\delta_{NH}=2.00$; $\delta_{CH_3}=-3.08$	$J_{3NH}=2.7$
CHO	H	H	CH_3		6.93	5.99		$\delta_{CHO}=9.30$; $\delta_{CH_3}=2.28$	$J_{34}=3.75$; $J_{3CH_3}=0.45$; $J_{4CH_3}=0.65$
H	CH_3	$COOC_2H_5$	H	6.47			7.30	$\delta_{CH_3}=2.24$	$J_{25}=2.20$; $J_{2CH_3}=1.00$; $J_{5NH_3}=3.05$
CH_3	SCN	SCN	CH_3					$\delta_{CH_3}=2.30$	

三、呋喃衍生物的^{1}H-NMR 化学位移和偶合常数

呋喃衍生物的^{1}H-NMR 化学位移计算如下[48,66]：



$$\delta_{H_2}=7.38+Z_{i2}$$
$$\delta_{H_3}=6.30+Z_{i3}$$
$$\delta_{H_4}=6.30+Z_{i4}$$
$$\delta_{H_5}=7.38+Z_{i5}$$

2-或 5-取代基 ($i=2$ 或 5)	$Z_{23}=Z_{54}$	$Z_{24}=Z_{53}$	$Z_{25}=Z_{52}$	2-或 5-取代基 ($i=2$ 或 5)	$Z_{23}=Z_{54}$	$Z_{24}=Z_{53}$	$Z_{25}=Z_{52}$
—H	0	0	0	$—SCH_3$	−0.12	−0.06	−0.09
$—CH_3$	−0.42	−0.12	−0.17	—SCN	0.40	0.06	0.10
$—CH_2OH$	−0.11	−0.05	−0.08	—CHO	0.93	0.31	0.34
$—CH_2NH_2$	−0.24	−0.06	−0.10	$—COCH_3$	0.81	0.23	0.19
—CH=CHCHO	0.70	0.35	0.42	$—COCF_3$	1.34	0.50	0.64
—Br	−0.02	0.03	−0.01	—COOH	0.94	0.33	0.41
—I	0.12	−0.13	−0.01	$—COOCH_3$	0.85	0.22	0.25
$—OCH_3$	−1.34	−0.23	−0.68	—COCl	1.20	0.39	0.48
$—NO_2$	1.21	0.55	0.51	—CN	0.85	0.32	0.28

续表

3-或4-取代基 (i=3或4)	$Z_{32}=Z_{45}$	$Z_{34}=Z_{43}$	$Z_{35}=Z_{42}$	3-或4-取代基 (i=3或4)	$Z_{32}=Z_{45}$	$Z_{34}=Z_{43}$	$Z_{35}=Z_{42}$
—H	0	0	0	—CHO	0.48	0.37	-0.07
—CH_3	-0.27	-0.17	-0.15	—$COCH_3$	0.46	0.36	-0.12
—I	-0.13	0.04	-0.22	—COOH	0.89	0.54	0.36
—OCH_3	-0.46	-0.28	-0.37	—$COOCH_3$	0.45	0.33	-0.14
—SCH_3	-0.18	-0.05	-0.15	—CN	0.45	0.22	-0.02
—SCN	0.19	0.19	0.03				

表 4-45　2-取代呋喃衍生物的^{1}H-NMR化学位移和偶合常数[48]

R	δ_3	δ_4	δ_5	J_{34}	J_{35}	J_{45}	其　他
CH_3	5.83	6.12	7.15	3.4	1.0	1.9	$\delta_{CH_3}=2.17$ $J_{3CH_3}=-1.1$ $J_{4CH_3}=0.4$ $J_{5CH_3}=-0.35$
CH_2OH	6.29	6.37	7.48	3.17	0.84	1.90	
CH_2SH	6.17	6.29	7.37	3.25	0.73	1.91	$\delta_{CH_2}=3.66$; $\delta_{SH}=1.98$ $J_{3CH_2}=0.79$ $J_{CH_2,SH}=7.4$
CH_2NH_2	6.20	6.34	7.43	3.18	0.76	1.94	$J_{3,CH_2}=0.84$
OCH_3	4.96	6.07	6.70	3.15	1.15	2.15	
SCH_3	6.18	6.24	7.29	3.20	0.85	1.95	
CN	6.86	6.36	7.38	3.55	0.70	1.75	
$COCH_3$	6.96	6.33	7.33	3.45	0.75	1.70	
CHO	7.03	6.42	7.49	3.55	0.80	1.70	$J_{4,CHO}=0.45$ $J_{5,CHO}=0.45$
$COCF_3$	7.64	6.80	8.02	3.70	0.76	1.70	
COOH	7.24	6.63	7.79	3.51	0.86	1.73	
$COOCH_3$	6.98	6.30	7.34	3.40	0.85	1.70	
$COOC_2H_5$	7.22	6.63	7.80	3.47	0.91	1.76	
COCl	7.52	6.70	7.88	3.79	0.79	1.70	
Br	6.15	6.21	7.25	3.25	0.80	2.10	
I	6.42	6.17	7.37	3.25	0.95	1.95	
NO_2	7.51	6.85	7.89	3.66	0.98	1.92	
SCN	6.70	6.36	7.48	3.40	0.85	1.95	
CH═CH—COOH	6.85	6.59	7.70	3.44		1.84	
CH═CH—CHO	7.00	6.65	7.80	3.41	0.75	1.81	$J_{5,—CH(\alpha)}=0.38$
$COCH_2CH_2OCOCH_3$	7.40	6.70	7.87	3.60	0.82	1.72	
CH═C$(CN)_2$	7.43	6.80	7.98	3.75	0.70	1.65	$\delta_{—CH}=7.88$ $J_{3,—CH}=-0.40$ $J_{4,—CH}=+0.40$ $J_{5,—CH}=+0.50$
CH═NC_6H_5	6.91	6.41	7.48	3.50	0.80	1.75	$\delta_{—CH}=8.18$ $J_{3,—CH}=-0.35$ $J_{4,—CH}=+0.40$ $J_{5,—CH}=+0.20$
CH═$CHCOCH_3$	6.58	6.42	7.44	3.5	0.5	1.8	
—COCH═CH—	7.17	6.50	7.54	3.5	0.8	1.7	
	6.64	6.43	7.45	3.4		1.8	

表 4-46 3-取代呋喃衍生物的^{1}H-NMR 化学位移和偶合常数[48]

R	δ_3	δ_4	δ_5	J_{24}	J_{25}	J_{45}	其　　他
CH_3	7.03	6.06	7.14	0.85	1.55	1.75	$J_{2,CH_3}=-0.95$ $J_{4,CH_3}=-0.45$ $J_{5,CH_3}=0.40$
OCH_3	6.92	6.02	7.01	1.00	1.65	1.90	
SCH_3	7.20	6.25	7.23	0.80	1.50	1.85	
CN	7.83	6.52	7.36	0.75	1.55	1.95	
$COCH_3$	7.84	6.66	7.26	0.75	1.40	1.80	
CHO	7.86	6.67	7.31	0.80	1.45	1.90	$J_{2,CHO}=0.40$ $J_{5,CHO}=0.75$
$COOCH_3$	7.83	6.63	7.24	0.70	1.55	1.85	
I	7.25	6.34	7.16	0.70	1.50	1.90	
SCN	7.57	6.49	7.41	0.85	$J_{25}+J_{45}=3.55$		
HgCl	7.33	6.40	7.67	0.6	1.3	1.7	$J_{2,Hg}=48.4$ $J_{4,Hg}=74$ $J_{5,Hg}=27.9$
COOH	8.27	6.84	7.74	0.8	1.5	1.8	

表 4-47 2,3-二取代呋喃衍生物的^{1}H-NMR 化学位移和偶合常数

R^2	R^3	δ_4	δ_5	J_{45}	
CH_3	COOH	6.74	7.49	1.94	
COOF	COOH	7.09	7.99	1.83	
Br	CH_3	6.24	7.32	2.0	$\delta_{CH_3}=2.00$
Br	CH_2Br	6.36	7.31	2.1	$\delta_{CH_2}=4.14$
$COOCH_3$	CH_3	6.28	7.37	1.9	$\delta_{CH_3}=2.28$; $\delta_{OCH_3}=3.78$
$COOCH_3$	CH_2Br	6.55	7.46	2.1	$\delta_{CH_2}=4.65$; $\delta_{OCH_3}=3.85$
$COOCH_3$	CH_2CN	6.72	7.66	2.1	$\delta_{CH_2}=4.01$; $\delta_{OCH_3}=3.92$
CHO	CH_3	6.38	7.50	1.6	$\delta_{CHO}=9.71$; $\delta_{CH_3}=2.36$; $J_{4,CHO}=0.4$; $J_{4,CH_3}=J_{5,CHO}=J_{5,CH_3}=0.5$
$COCH_3$	OH	6.23	7.23	2.0	$\delta_{OH}=8.95$; $\delta_{CH_3}=2.35$
$COCH_3$	OCH_3	6.25	7.28	2.0	$\delta_{CH_3}=2.28$; $\delta_{OCH_3}=3.88$

表 4-48 2,4-二取代呋喃衍生物的^{1}H-NMR 化学位移和偶合常数[48]

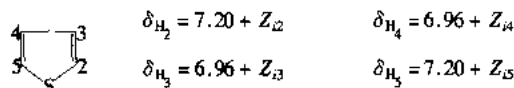
R^2	R^4	δ_3	δ_5	J_{35}	
CHO	CH_3	7.01	7.42	0.9	$\delta_{CHO}=9.53$; $\delta_{CH_3}=2.09$ $J_{3,CH_3}=0.5$; $J_{5,CHO}=1.1$; $J_{5,CHO}=0.5$
CN	CH_3	6.86	7.29	0.8	$\delta_{CH_3}=2.08$; $J_{3,CH_3}=0.4$; $J_{5,CH_3}=1.1$

表 4-49 2,5-二取代呋喃衍生物的^{1}H-NMR 化学位移和偶合常数[48,61]

R^2	R^5	δ_3	δ_4	J_{34}	
CH_3	CH_3	5.69	5.69	—	$\delta_{CH_3}=2.14$; $J_{3,CH_3}=0.3,0.4$; $J_{4,CH_3}=0.3,0.4$
$COOCH_3$	CH_2Br	7.05	6.46	3.5	$\delta_{CH_2}=4.47$; $J_{3,CH_2}=0.4$; $J_{4,CH_2}=0.5$
$COOC_2H_5$	CH_3	6.95	6.04	3.3	$\delta_{CH_3}=2.37$; $J_{3,CH_3}=0.5$; $J_{4,CH_3}=0.9$
$COOC_2H_5$	Br	7.06	6.41	3.4	
$COOC_2H_5$	Cl	7.09	6.27	3.4	
$COOC_2H_5$	CH_2Cl	7.04	6.44	3.5	$\delta_{CH_2}=4.56$; $J_{3,CH_2}=0.3$; $J_{4,CH_2}=0.5$
CHO	CH_2Cl	7.42	6.77	3.67	
CHO	CH_3	7.05	6.17	3.4	$\delta_{CHO}=9.45$; $\delta_{CH_3}=2.38$; $J_{3,CH_3}=0.4$; $J_{4,CH_3}=0.9$; $J_{4,CHO}=0.3$
CH—CHCHO	$CH_2C\equiv CH$	6.63	6.33	3.5	$J_{4,CH_2}=1.2$

四、噻吩衍生物的^{1}H-NMR化学位移和偶合常数

噻吩衍生物的^{1}H-NMR化学位移计算[1,48,66]如下：



$$\delta_{H_2}=7.20+Z_{i2} \qquad \delta_{H_4}=6.96+Z_{i4}$$

$$\delta_{H_3}=6.96+Z_{i3} \qquad \delta_{H_5}=7.20+Z_{i5}$$

2-或5-取代基（i=2或5）	$Z_{23}=Z_{54}$	$Z_{24}=Z_{53}$	$Z_{25}=Z_{52}$	2-或5-取代基（i=2或5）	$Z_{23}=Z_{54}$	$Z_{24}=Z_{53}$	$Z_{25}=Z_{52}$
—H	0	0	0	—SCH_3	-0.03	-0.18	-0.05
—CH_3	-0.36	-0.24	-0.29	—SCN	0.30	-0.05	0.28
—C≡CH	0.15	-0.16	-0.12	—SO_2CH_3	1.03	0.20	0.79
—Cl	-0.25	-0.22	-0.22	—SO_2Cl	0.73	0.06	0.45
—Br	-0.05	-0.27	-0.11	—CHO	0.65	0.10	0.45
—I	0.13	-0.33	0.01	—$COCH_3$	0.57	0.00	0.28
—OH①	-0.72	0.59	-3.10	—COOH	0.80	0.08	0.40
—OCH_3	-0.94	-0.43	-0.82	—$COOCH_3$	0.70	-0.05	0.20
—NH_2	-0.95	-0.45	-0.85	—COCl	0.88	0.06	0.44
—NO_2	0.82	-0.03	0.30	—CN	0.47	0.00	0.28
—SH	0.00	-0.20	-0.07				

① 以酮式存在。

3-或4-取代基（i=3或4）	$Z_{32}=Z_{45}$	$Z_{34}=Z_{43}$	$Z_{35}=Z_{42}$	3-或4-取代基（i=3或4）	$Z_{32}=Z_{45}$	$Z_{34}=Z_{43}$	$Z_{35}=Z_{42}$
—H	0	0	0	—SCH_3	-0.33	-0.10	-0.03
—CH_3	-0.45	-0.22	-0.14	—SCN	0.25	0.05	0.05
—Cl	-0.22	-0.11	-0.03	—SO_2CH_3	0.96	0.48	0.46
—Br	-0.12	-0.08	-0.10	—CHO	0.79	0.45	0.03
—I	0.06	0.00	-0.19	—$COCH_3$	0.68	0.47	-0.02
—OCH_3	-1.10	-0.38	-0.20	—COOH	0.99	0.48	0.24
—NH_2	-1.25	-0.53	-0.25	—$COOCH_3$	0.78	0.47	-0.05
—NO_2	0.95	0.60	0.03	—COCl	1.05	0.50	0.03
—SH	-0.22	-0.20	-0.10	—CN	0.63	0.20	0.15

表 4-50　2-取代噻吩衍生物的^{1}H-NMR化学位移和偶合常数[48]

R	δ_3	δ_4	δ_5	J_{34}	J_{35}	J_{45}	R	δ_3	δ_4	δ_5	J_{34}	J_{35}	J_{45}
CH_3	6.63	6.75	6.91	3.46	1.16	5.20	COOH	7.76	7.04	7.60	3.5	1.2	4.9
OCH_3	6.11	6.59	6.41	3.7	1.8	5.2	SO_2CH_3	7.99	7.16	7.99	3.9	—	4.7
Br	6.93	6.73	7.05	3.62	1.39	5.63	NO_2	7.88	7.11	7.59	3.8	1.5	5.4
$COCH_3$	7.64	7.09	7.64	3.7	—	5.1	Cl	6.79	6.74	6.92	3.71	1.48	5.60
CHO	7.99	7.14	7.79	3.7	—	5.0		7.13	6.66	7.18	3.56	1.25	5.41

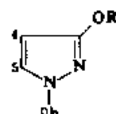
表 4-51　3-取代噻吩衍生物的^{1}H-NMR化学位移和偶合常数[48]

R	δ_3	δ_4	δ_5	J_{34}	J_{35}	J_{45}	R	δ_3	δ_4	δ_5	J_{34}	J_{35}	J_{45}
CH_3	6.75	6.77	7.05	1.28	2.94	4.88	$COCH_3$	8.34	7.74	7.54	1.4	2.7	5.1
OCH_3	6.06	6.66	6.94	1.6	3.1	5.0	CHO	8.16	7.59	7.59	1.5	2.4	—
SCH_3	6.86	6.86	7.14	—	2.8	5.2	COOH	8.19	7.44	7.44			—
Br	7.35	7.04	7.37	1.2	3.2	5.2	SO_2CH_3	8.16	7.44	7.66	1.4	2.8	4.9

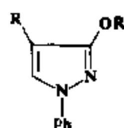
表 4-52　2,3-二取代噻吩衍生物的^{1}H-NMR 化学位移和偶合常数[62]

	R	H_5	H_4	$J_{4,5}$		R	H_5	H_4	$J_{4,5}$
(噻吩, S; -OR, -$COCH_3$)	*t*-Bu	7.38	6.87	5.5	(噻吩, S; -COMe, -OR)	*t*-Bu	6.51	7.09	6.2
	H	7.34	6.70	5.3		H	6.25	6.65	6.7
(噻吩, S; -OR, -COOEt)	*t*-Bu	7.25	6.73	5.3	(噻吩, S; -COOEt, -OR)	*t*-Bu	6.55	7.10	6.1
	H	7.27	6.67	5.3		H	6.24	6.85	6.0

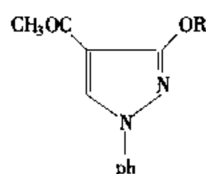
五、其他五元芳杂环化合物的^{1}H-NMR 化学位移和偶合常数



OR	δ_{4H}	J_{45}	δ_{5H}	OR	δ_{4H}	J_{45}	δ_{5H}
OH,10.24	5.59	3.0	8.25	OCH_3,3.95	5.86	2.5	7.67
$OCOCH_3$,2.31	6.36	2.7	7.84	OCH_2,4.78;$=CH_2$	5.92	2.9	7.69



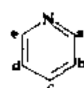
R	δ_{5H}	δ_{OH}	R	δ_{5H}	δ_{OH}
CH_3,1.92	7.99	9.75	CH_2,6.35;		
NO_2	9.36	12.11	NC_5H_{10},1.50,2.48		
NH_2,5.54	7.49	5.54	CH_3,1.96;CH,3.77;	6.97	11.62
Br	9.53	10.99	C_6H_{11},2.00~1.50		
Cl	9.55	11.01	CH_2,3.29;$=CH_2$,5.17;	7.45	11.11
$C_6H_5N=N$,7.50~7.10	9.40	9.72	CH,6.00		
$CH_2NC_5H_{10}$	9.12	5.60			



R	δ_{OR}	δ_{COCH_3}	δ_{5H}
H	11.11	2.43	8.88
CH_3	4.08	2.48	8.23

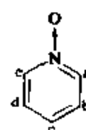
第七节　六元芳杂环化合物的^{1}H-NMR 化学位移和偶合常数

一、一般六元芳杂环化合物的^{1}H-NMR 化学位移和偶合常数[66]

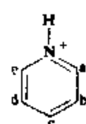


(a,e) 8.60
(b,d) 7.25
(c) 7.64

$J_{ab}=5.5$	$J_{ab}=4\sim6$
$J_{ac}=1.9$	$J_{ac}=0\sim2.5$
$J_{ad}=0.9$	$J_{ad}=0\sim2.5$
$J_{ae}=0.4$	$J_{ae}=0\sim0.6$
$J_{bc}=7.6$	$J_{bc}=7\sim9$
$J_{bd}=1.6$	$J_{bd}=0.5\sim2$

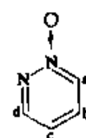


(a,e) 8.10
(b,d) 7.28
(c) 7.08



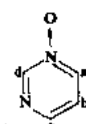
(a,e) 9.23　(b,d) 8.50　(c) 9.04

$J_{ab}=6.0$　$J_{ac}=1.5$　$J_{ad}=0.8$　$J_{ae}=1.0$　$J_{bc}=8.0$　$J_{bd}=1.4$



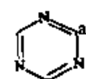
(a) 8.26　(b) 7.83　(c) 7.22　(d) 8.54

$J_{ab}=6.5$　$J_{ac}=1.0$　$J_{ad}=1.0$　$J_{bc}=8.0$　$J_{bd}=2.5$

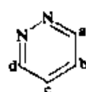


(a) 8.43　(b) 7.34　(c) 8.24　(d) 8.98

$J_{ab}=6.8$　$J_{ac}=1.6$　$J_{ad}=2.0$　$J_{bc}=4.9$　$J_{bd}=1.0$　$J_{cd}=0$

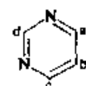


(a) 9.25



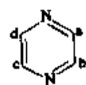
(a,d) 9.24　(b,c) 7.55

$J_{ab}=4.9$　$J_{ac}=2.0$　$J_{ad}=3.5$　$J_{bc}=8.4$



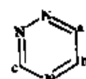
(a,c) 8.78　(b) 7.36　(d) 9.26

$J_{ab}=5.0$　$J_{ac}=2.5$　$J_{ad}=1.5$　$J_{bd}=0$



(a) 8.63

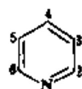
$J_{ab}=1.8$　$J_{ac}=1.8$　$J_{ad}=0.5$



(a) 9.48　(b) 8.84　(c) 9.88

二、吡啶衍生物的^{1}H-NMR化学位移和偶合常数

取代基对吡啶环氢化学位移的影响情况[66]如下：



$\delta_2=8.59+Z_{i2}$
$\delta_3=7.38+Z_{i3}$
$\delta_4=7.75+Z_{i4}$
$\delta_5=7.38+Z_{i5}$
$\delta_6=8.59+Z_{i6}$

2-或6-取代基（$i=2$或6）	$Z_{23}=Z_{65}$	$Z_{24}=Z_{64}$	$Z_{25}=Z_{63}$	$Z_{26}=Z_{62}$	2-或6-取代基（$i=2$或6）	$Z_{23}=Z_{65}$	$Z_{24}=Z_{64}$	$Z_{25}=Z_{63}$	$Z_{26}=Z_{62}$
—H	0	0	0	0	—O—n—C_4H_9	-0.53	-0.03	-0.49	-0.32
—CH_3	-0.11	-0.01	-0.16	0.08	—NH_2	-0.68	-0.31	-0.78	-0.48
—CH_2CH_3	-0.09	-0.08	-0.15	0.03	—$NHCOCH_3$	0.94	0.16	-0.20	-0.10
—CH_2—苯基	0.12	-0.08	-0.20	0.02	—$NHCOOCH_2CH_3$	0.59	0.07	-0.24	-0.21
—CH_2OH	0.37	0.30	0.02	0.06	—$NHNO_2$	0.34	0.31	-0.03	-0.41
—CH_2NH_2	0.20	0.07	-0.09	0.05	—NO_2	1.09	0.67	0.74	0.26
—$CH_2SC_3H_7$	0.04	-0.08	-0.26	-0.06	—CHO	0.93	0.42	0.50	0.44
—CH_2SO_2—苯基	0	-0.3	0	-0.2	—$COCH_3$	0.82	0.37	0.39	0.28
—CH═CH_2	0.11	-0.14	-0.11	0.04	—CO—苯基	0.62	0.55	0.32	0.28
—苯基	0.16	-0.28	-0.40	-0.03	—COOH	0.97	0.43	0.48	0.42
2-吡啶基	1.12	-0.09	-0.26	0.00	—COO—n—C_4H_9	0.86	0.39	0.35	0.35
—F	-0.10	0.40	0.12	-0.13	—$CONH_2$	1.05	0.47	0.43	0.30
—Cl	0.32	0.29	0.29	0.20	—$CSNH_2$	1.41	0.37	0.33	0.25
—Br	0.41	0.17	0.19	0.02	—CH═NOH	0.40	0.28	0.01	0.16
—OH	-0.7	0.0	-1.0	-0.9	—CN	0.88	0.38	0.55	0.39

3-或5-取代基（$i=3$或5）	$Z_{32}=Z_{56}$	$Z_{34}=Z_{54}$	$Z_{35}=Z_{53}$	$Z_{36}=Z_{52}$	3-或5-取代基（$i=3$或5）	$Z_{32}=Z_{56}$	$Z_{34}=Z_{54}$	$Z_{35}=Z_{53}$	$Z_{36}=Z_{52}$
—H	0	0	0	0	—$NHCOCH_3$	0.37	0.50	0.06	-0.16
—CH_3	-0.02	-0.06	-0.09	-0.02	—SO_3H	0.70	1.14	0.81	0.70
—CH_2OH	0.11	0.15	0.04	-0.04	—CHO	0.45	0.42	0.12	0.20
—CH_2NH_2	0.16	0.13	0.04	0.00	—$COCH_3$	0.72	0.68	0.30	0.37
—CH_2SO_2—苯基	-0.24	-0.15	-0.22	0.01	—CO—苯基	0.47	0.54	0.37	0.34
—CH═CHCOOH	0.45	0.52	0.34	0.17	—$COOCH_3$	0.62	0.60	0.23	0.34
—Cl	0.20	0.24	0.19	0.09	—$CSNH_2$	0.68	0.67	0.24	0.26
—Br	0.20	0.43	0.34	0.18	—CH═NOH	0.39	0.43	0.19	0.15
—OH	-0.03	-0.37	0.15	-0.24	—CN	0.63	0.72	0.43	0.50
—NH_2	-0.06	-0.49	0.02	-0.36					

续表

4-取代基 ($i=4$)	$Z_{42}=Z_{46}$	$Z_{43}=Z_{45}$	4-取代基 ($i=4$)	$Z_{42}=Z_{46}$	$Z_{43}=Z_{45}$
—H	0	0	—NH_2	-0.15	-0.74
—CH_3	0.01	-0.10	—$NHCOCH_3$	-0.05	0.31
—CH_2—苯基	0.00	-0.15	—SCH_2—苯基	-0.02	0.04
—CH_2OH	0.07	0.14	—S—苯基	0.05	-0.16
—CH_2NH_2	0.01	0.03	—CHO	0.47	0.58
—CH_2S—n—C_3H_7	-0.06	-0.13	—$COCH_3$	0.40	0.58
—CH_2SO_2—苯基	-0.09	-0.18	—CO—苯基	0.36	0.40
—CH=CH_2	0.12	0.13	—COO—n—C_4H_9	0.34	0.54
—Cl	0.00	0.05	—$CSNH_2$	0.35	0.68
—Br	0.09	0.35	—CH=NOH	0.24	0.37
—OCH_3	0.02	-0.29	—CN	0.46	0.62

表 4-53　2,3-二取代吡啶衍生物的 ^{1}H-NMR 化学位移和偶合常数[48]

R^2	R^3	δ_4	δ_5	δ_6	J_{45}	J_{46}	J_{56}	其　他
CH_3	CH_3	0.29	0.00	1.38	7.35	1.3	5.0	
CH_3	$COOC_2H_5$	8.31	7.43	8.75	7.9	1.8	4.9	$\delta_{CH_2}=4.42$ $\delta_{CH_3}=2.71, 1.37$ $J_{CH_2,CH_3}=7.2$
CH_3	$COCH_3$	8.32	7.45	8.69	7.9	1.7	4.8	
CH_3	CN	8.18	7.38	8.78	8.2	1.5	4.9	
CH_3	OH	7.39	7.28	8.06	6.8	0.8	4.6	$\delta_{OH}=8.7$；$\delta_{CH_3}=2.47$
OH	CH_3	7.41	6.20	7.41	6.7	0.0	6.7	$\delta_{OH}=12$；$\delta_{CH_3}=2.05$ $J_{4,CH_3}=0.5$
OH	NO_2	8.58	6.48	8.03	7.5	1.7	6.6	$\delta_{OH}=12.9$
NH_2	NH_2	6.96	6.56	7.58	7.5	1.7	4.9	$\delta_{NH_2}=5.22$
NH_2	CH_3	7.28	6.54	7.99	7.4	1.7	4.8	$\delta_{NH_2}=5.91$ $\delta_{CH_3}=2.09$ $J_{4,CH_3}=0.7$
Cl	Cl	8.22	7.61	8.57	7.3	1.7	4.8	
Cl	NH_2	7.38	7.15	7.90	7.9	1.9	4.4	$\delta_{NH_2}=5.44$

表 4-54　2,4-二取代吡啶衍生物的 ^{1}H-NMR 化学位移和偶合常数[63]

	δ_3	δ_5	δ_6	δ_{CH_3}	J_{35}	J_{36}	J_{56}
$R^2=R^4=CH_3$	7.11	7.07	8.43	2.46, 2.27	<0.5	1.4	5.6
$R^2=CH_3$, $R^4=COON_3$	2.40	2.46	3.26	-2.66	<0.5	1.0	4.6

表 4-55　2,5-二取代吡啶衍生物的 ^{1}H-NMR 化学位移和偶合常数[63]

R^2	R^5	δ_3	δ_4	δ_6	J_{34}	J_{36}	J_{46}	其　他
CH_3	C_2H_5	7.17	7.57	8.41	8.1	0.7	2.4	$\delta_{CH_3}=1.16, 2.47$；$J_{CH_2\cdot CH_3}=7.5$
CH_3	CH=CH_2	7.24	7.87	8.76	8.1	0.5	2.0	$\delta_{CH_3}=2.55$
CH_3	OH	7.15	7.23	8.23	8.7	0.6	2.3	$\delta_{OH}=8.8$；$\delta_{CH_3}=2.50$
OH	COOH	6.53	7.98	8.22	9.7	<0.3	2.6	$\delta_{OH}=11.5$；$\delta_{COOH}=11.5$
OC_4H_9	NO_2	7.07	8.59	9.18	9.1	<0.3	2.8	$\delta_{OCH_2}=4.46$；$\delta_{CH_2CH_2}=1.63$；$\delta_{CH_3}=98$； $J_{OCH_2\cdot CH_2}=6.2$；$J_{CH_2\cdot CH_3}=6.0$
NH_2	Cl	6.63	7.49	8.05	9.0	<0.3	2.5	$\delta_{NH_2}=6.20$
Cl	Cl	7.68	8.13	8.70	9.0	<0.3	3.0	
Br	Br	7.71	8.08	8.63	8.3	<0.3	2.5	

表 4-56 对称 2,6-二取代吡啶衍生物的^{1}H-NMR 化学位移和偶合常数[48]

$R^2=R^6$	δ_3	δ_4	J_{34}	其他	$R^2=R^6$	δ_3	δ_4	J_{34}	其他
D	0.00	0.37	7.7		OH	6.35	8.03	8.4	$\delta_{OH}=11.4$
CH_3	7.04	7.59	8.2	$\delta_{CH_3}=2.44$	NH_2	5.90	7.22	7.8	$\delta_{NH_2}=5.54$
CN	8.49	8.52	≈8		$CSNH_2$	8.93	8.29	7.8	$\delta_{NH_2}=10.6$

表 4-57 非对称 2,6-二取代吡啶衍生物的^{1}H-NMR 化学位移和偶合常数[63]

R^2	R^6	δ_3	δ_4	δ_5	J_{34}	J_{35}	J_{45}	其他
CH_3	CH_2OH	7.65	7.81	7.16	8.1	0.7	7.8	$\delta_{OH}=5.73$;$\delta_{CH_2}=4.74$
CH_3	CH_2NH_2	7.31	7.68	7.13	7.3	1.0	7.8	$\delta_{CH_2}=3.89$;$\delta_{NH_2}=2.0$
CH_3	CH_2NHCH_3	7.36	7.66	7.12	7.4	0.9	7.9	$\delta_{CH_2}=3.77$;$\delta_{CH_3}=2.47$;$\delta_{NH}=2.37$
CH_3	CH=NOH	7.80	7.73	7.35	8.1	0.6	8.3	$\delta_{OH}=12.00$;$\delta_{=CH}=8.29$;$\delta_{CH_3}=2.58$
CH_3	CN	7.76	7.95	8.09	8.0	1.2	7.8	$\delta_{CH_3}=2.63$
CH_3	$COCH_3$	7.56	7.87	7.95	7.5	1.3	7.4	
CH_3	CHO	7.65	7.92	8.07	7.7	1.5	7.6	$\delta_{CHO}=10.15$
CH_3	COOH	7.82	8.13	8.27	≈8	≈1	≈8	$\delta_{COOH}=6.19$;$\delta_{CH_3}=2.75$
CH_3	$COOC_4H_9$	7.60	7.90	8.05	≈8	≈1	≈8	$\delta_{OCH_2}=4.39$;$\delta_{CH_2CH_3}=1.65$; $\delta_{CH_3}=0.95$
CH_3	$CSNH_2$	7.61	8.01	8.61	7.9	1.4	7.7	$\delta_{NH_2}=10.3$;$\delta_{CH_3}=2.66$

表 4-58 3,5-二取代吡啶衍生物的^{1}H-NMR 化学位移和偶合常数

R^3	R^5	δ_2	δ_4	J_{24}	
Cl	Cl	8.71	8.23	1.4	
CN	CN	9.30	8.95	2.0	
$COOCH_3$	$COOCH_3$	9.24	8.69	2.0	$\delta_{OCH_3}=4.63$

表 4-59 三取代吡啶衍生物的^{1}H-NMR 化学位移和偶合常数①[48]

R^2	R^3	R^6	δ_4	δ_5	J_{45}	
CH_3	$COCH_3$	CH_3	8.17	7.24	8.4	$J_{5,CH_3}=0.5$
CH_3	COOH	CH_3	8.26	7.27	8.1	$\delta_{COOH}=11.30$ $\delta_{CH_3}=2.47$ $J_{5,CH_3}=0.5$
CH_3	$COCH_3$	C_6H_5	8.36	8.15	8.4	$\delta_{COCH_3}=2.65$
CH_3	COOH	C_6H_5	8.53	8.18	8.8	$\delta_{COOH}=12.03$ $\delta_{CH_3}=3.14$
CH_3	$COCH_3$	OH	8.03	6.32	9.7	$\delta_{OH}=12.2$ $\delta_{COCH_3}=2.61$

① $R^2=CH_3$,$R^4=R^6=CHO$:$\delta_3=7.82$,$\delta_4=7.93$,$\delta_{CHO}=9.22,9.70$,$\delta_{CH_3}=2.46$,$J_{35}<0.5$

$R^2=R^4=CH_3$,$R^6=COOH$:$\delta_3=7.36$;$\delta_5=7.87$,$\delta_{COOH}=10.44$,$\delta_{CH_3}=2.40$,$J_{35}<0.5$

三、二氮杂苯衍生物的¹H-NMR化学位移和偶合常数

表 4-60 邻二氮杂苯、对二氮杂苯和嘧啶的¹H-NMR化学位移和偶合常数[64]

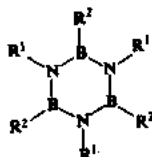
参数	邻二氮杂苯	对二氮杂苯	嘧啶	参数	邻二氮杂苯	对二氮杂苯	嘧啶
δ_2		8.63	9.26	J_{26}		≈0.5	≈0
δ_3	9.24	8.63		J_{34}	4.9		
δ_4	7.54		9.78	J_{35}	2.0	≈0.5	
δ_5	7.54	8.63	7.36	J_{36}	3.5	1.8	
δ_6	9.24	8.63	9.78	J_{45}	8.4		5.0
J_{23}		1.8		J_{46}	2.0		2.5
J_{24}			≈0	J_{56}	4.9	1.8	5.0
J_{25}		1.8	1.5				

四、其他氮杂苯衍生物的¹H-NMR化学位移和偶合常数

表 4-61 硼嗪及其衍生物的¹H-NMR化学位移和偶合常数[65]

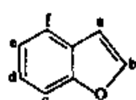
化合物	取代基		化学位移	偶合常数
	R^1	R^2		
1	H	H	$\delta_{NH}=5.49$	$J_{HN^{14}}=56$
			$\delta_{BH}=4.51$	$J_{HB^{11}}=138$
2	H	Cl	$\delta_{NH}=5.37$	
3	CH_3	Cl	$\delta_{NCH_3}=3.11$	
4	CH_2CH_3	Cl	$\delta_{NCH_2}=3.64$	$J_{NCH_2CH_3}=8$
			$\delta_{CH_3}=1.06$	
5	CH_3	H	$\delta_{NCH_3}=3.04$	$J_{H,B}=125$
6	CH_3	CH_3	$\delta_{NCH_3}=3.02$	
			$\delta_{BCH_3}=0.44$	
7	CH_2CH_3	CH_3	$\delta_{BCH_3}=0.51$	
			$\delta_{NCH_2}=3.42$	
			$\delta_{CH_3}=1.04$	

化合物	取代基		化学位移	偶合常数
	R^1	R^2		
8	CH_3	CH_2CH_3	$\delta_{NCH_3}=2.94$	$J_{CH_3,N}=3.0$
			$\delta_{BCH_2}=0.99$	
			$\delta_{BCH_3}=0.99$	
9	CH_2CH_3	CH_2CH_3	$\delta_{NCH_2}=3.61$	
			$\delta_{CH_3}=1.04$	
			$\delta_{BCH_2}=0.92$	
10	C_6H_5	CH_3	$\delta_{BCH_3}=0.16$	
			$\delta_{Ph}=7.19$	
11	C_6H_5	CH_2CH_3	$\delta_{BCH_2}=0.41$	
			$\delta_{Ph}=7.19$	



第八节 稠合芳杂环化合物的¹H-NMR化学位移和偶合常数

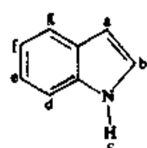
一、部分稠合芳杂环化合物的¹H-NMR化学位移和偶合常数[66]



(a) 6.66
(b) 7.52
(c) 7.42
(d) 7.19
(e) 7.13
(f) 7.49

$J_{ab}=2.5$
$J_{ac}=0.9$
$J_{ad}=J_{ae}=J_{af}=0$
$J_{bc}=J_{bd}=J_{be}=J_{bf}=0$
$J_{cd}=8.4$

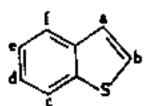
$J_{ce}=0.9$
$J_{cf}=0.8$
$J_{de}=7.3$
$J_{df}=1.2$
$J_{ef}=7.9$



(a) 6.45
(b) 7.26
(c) 10.1
(d) 7.40
(e) 7.09
(f) 6.99
(g) 7.55

$J_{ab}=3.1$
$J_{ac}=2.0$
$J_{ad}=0.7$
$J_{ae}=J_{af}=J_{ag}=0$
$J_{bc}=2.5$
$J_{bd}=J_{be}=J_{bf}=J_{bg}=0$

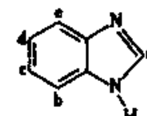
$J_{de}=8.1$
$J_{df}=1.3$
$J_{dg}=0.9$
$J_{ef}=7.1$
$J_{eg}=1.2$
$J_{fg}=7.8$



(a) 7.29
(b) 7.40
(c) 7.86
(d) 7.31
(e) 7.33
(f) 7.78

$J_{ab}=6$
$J_{ac}=\sim0.8$
$J_{ad}=J_{ae}=J_{af}=0$
$J_{bc}=J_{bd}=J_{be}=J_{bf}=0$
$J_{cd}=9$

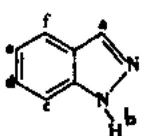
$J_{ce}=2.5$
$J_{cf}=0.7$
$J_{de}=7.2$
$J_{df}=2.5$
$J_{ef}=9$



(a) 8.08
(b,e) 7.70
(c,d) 7.26

$J_{bc}=J_{de}=8.2$
$J_{bd}=J_{ce}=1.4$

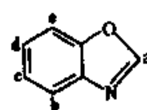
$J_{be}=0.7$
$J_{cd}=7.1$



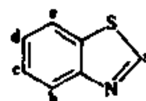
(a) 8.20
(b) 12.4
(c) 7.60
(d) 7.34
(e) 7.20
(f) 7.85

$J_{ac}=0.8$
$J_{ad}=J_{ae}=J_{af}=0$
$J_{cd}=7.9$
$J_{ce}=1.2$

$J_{cf}=1.0$
$J_{de}=7.0$
$J_{df}=1.2$
$J_{ef}=7.8$

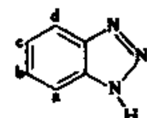


(a) 8.1
(b), (c), (d), (e) 7.2 – 7.9



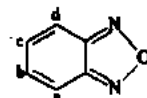
(a) 9.23
(b) 8.23
(c) 7.55
(d) 7.55
(e) 8.12

衍生物：$J_{bc}=8$
$J_{bd}=1.5$
$J_{be}=0.5$
$J_{cd}=7.5$
$J_{ce}=1.5$
$J_{de}=8$



(a,d) 7.98
(b,c) 7.45

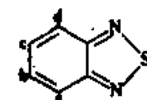
$J_{ab}=8.6$
$J_{ac}=0.8$
$J_{ad}=1.0$



(a,d) 7.64
(b,c) 7.24

$J_{ab}=9.3$
$J_{ac}=1.2$

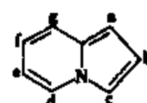
$J_{ad}=0.9$
$J_{bc}=6.4$



(a,d) 7.96
(b,c) 7.52

$J_{ab}=9.2$
$J_{ac}=1.0$

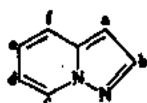
$J_{ad}=0.8$
$J_{bc}=6$



(a) 6.28
(b) 6.64
(c) 7.14
(d) 7.76
(e) 6.31
(f) 6.50
(g) 7.25

$J_{ab}=3.9$
$J_{ac}=1.2$
$J_{ad}=1.0$
$J_{bc}=2.7$
$J_{bg}=0.5$
$J_{cg}=0.5$

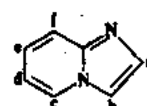
$J_{de}=6.8$
$J_{df}=1.0$
$J_{dg}=1.2$
$J_{ef}=6.4$
$J_{eg}=1.0$
$J_{fg}=9.0$



(a) 6.38
(b) 7.80
(c) 8.39
(d) 6.62
(e) 6.97
(f) 7.44

$J_{ab}=2.2$
$J_{ac}=0.9$
$J_{be}=0.5$
$J_{cd}=6.9$
$J_{ce}=1.0$

$J_{cf}=1.0$
$J_{de}=7.0$
$J_{df}=1.2$
$J_{ef}=8.9$



(a) 7.48
(b) 7.48
(c) 8.09
(d) 6.65
(e) 7.03
(f) 7.51

$J_{ab}=1.0$
$J_{bc}=0.7$
$J_{cd}=6.9$
$J_{ce}=1.2$

$J_{cf}=1.0$
$J_{de}=6.8$
$J_{df}=1.0$
$J_{ef}=9.3$

Chemical shifts		Coupling constants	
(a) 8.68 (b) 11	(c) 8.99 (d) 9.19		
(a) 8.00 (b) 7.26 (c) 8.81 (d) 8.05	(e) 7.61 (f) 7.43 (g) 7.68	$J_{ab}=8.3$ $J_{ac}=1.8$ $J_{ad}=0.8$ $J_{bc}=4.3$ $J_{de}=8.2$	$J_{df}=1.1$ $J_{dg}=0.5$ $J_{ef}=6.8$ $J_{eg}=1.6$ $J_{fg}=8.2$
(a) 7.74 (b) 7.27	(c) 8.57 (d) 8.75	$J_{ab}=8.5$ $J_{ac}=1.1$ $J_{bc}=6.0$	
(a) 7.50 (b) 8.45 (c) 9.15 (d) 7.87	(e) 7.50 (f) 7.57 (g) 7.71	$J_{ab}=6.0$ $J_{ad}=0.8$ $J_{bc}=0.8$ $J_{cg}<0.5$ $J_{de}=8.2$ $J_{cd}=1.3$	$J_{df}=1.3$ $J_{dg}=0.9$ $J_{ef}=7.0$ $J_{eg}=1.1$ $J_{fg}=8.7$
(b) 8.14 (c) 8.77	$J_{ab}=7.0$ $J_{bc}=1.7$		
(a) 7.73 (b) 9.10 (c) 8.30	(d) 7.57 (e) 7.57 (f) 7.57	$J_{ab}=5.7$ $J_{ac}=0.8$ $J_{cd}=8.6$ $J_{ce}=1.3$	$J_{cf}=0.8$ $J_{de}=6.9$ $J_{df}=1.5$ $J_{ef}=7.8$
(a) 9.29 (b) 9.23 (c) 8.01	(d) 7.83 (e) 7.58 (f) 7.84	$J_{ab}=0$ $J_{ac}=0.5$ $J_{cd}=8.5$ $J_{ce}=1.2$	$J_{cf}=0.8$ $J_{de}=6.9$ $J_{df}=1.2$ $J_{ef}=7.9$
(a,b) 8.74 (c,f) 8.07 (d,e) 7.68	$J_{ab}=1.8$ $J_{cd}=8.4$ $J_{ce}=1.6$ $J_{cf}=0.6$	$J_{de}=6.9$ $J_{df}=1.6$ $J_{ef}=8.4$	
(a,b) 9.44 (c,f) 7.93 (d,e) 7.85	$J_{ac}=0.4$ $J_{cd}=8.2$ $J_{ce}=1.2$	$J_{cf}=0.6$ $J_{de}=6.8$	
(a) 7.80 (b) 6.45 (c) 7.20 (d) 7.45 (e) 7.22 (f) 7.63	$J_{ab}=9.8$ $J_{cd}=8.5$ $J_{ce}=1.8$ $J_{cf}=0.0$	$J_{de}=8.6$ $J_{df}=2.0$ $J_{ef}=8.5$	
(a) 6.34 (b) 7.88 (c) 7.47 (d) 7.68 (e) 7.43 (f) 8.21	$J_{ab}=6.1$ $J_{cd}=8.4$ $J_{ce}=1.1$ $J_{cf}=0.5$	$J_{de}=7.0$ $J_{df}=1.8$ $J_{ef}=8.0$	

(a,b) 5.77 $J_{cd}=7.9$
(c,f) 6.52 $J_{ce}=1.5$
(d,e) 6.71 $J_{cf}=0.4$
$J_{de}=7.9$

(a,b) 6.42 $J_{cd}=7.8$
(c,f) 7.19 $J_{ce}=1.3$
(d,e) 7.12 $J_{cf}=1.1$
$J_{de}=7.1$

(a) 7.84 $J_{ab}=7.6$ $J_{bc}=7.3$
(b) 7.23 $J_{ac}=1.3$ $J_{bd}=0.9$
(c) 7.35 $J_{ad}=0.6$ $J_{cd}=8.5$
(d) 7.48

(a) 8.08 $J_{ab}=7.8$ $J_{bc}=7.2$
(b) 7.16 $J_{ac}=1.2$ $J_{bd}=0.9$
(c) 7.36 $J_{ad}=0.7$ $J_{cd}=8.2$
(d) 7.49 $J_{ae}=0.7$
(e) 10.3

(a) 8.36 $J_{ab}=8.0$ $J_{bc}=7.1$
(b) 7.38 $J_{ac}=1.8$ $J_{bd}=1.1$
(c) 7.73 $J_{ad}=0.5$ $J_{cd}=8.4$
(d) 7.50

(a) 8.27 $J_{ab}=8.2$ $J_{bc}=7.0$
(b) 7.27 $J_{ac}=1.4$ $J_{bd}=1.0$
(c) 7.74 $J_{ad}=0.4$ $J_{cd}=8.6$
(d) 7.57 $J_{ae}=0.4$
(e) 11.7

(a) 9.09 $J_{ab}=0.4$ $J_{be}=0.6$
(b) 8.19 $J_{ae}=0.9$ $J_{cd}=6.6$
(c) 7.64 $J_{bc}=8.2$ $J_{ce}=1.2$
(d) 7.89 $J_{bd}=1.4$ $J_{de}=9.0$
(e) 8.22

二、喹啉及其衍生物的¹H-NMR化学位移和偶合常数

表 4-62 喹啉及其部分衍生物的¹H-NMR化学位移和偶合常数

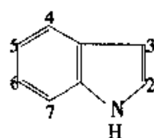
4: 7.95; 3: 7.24; 2: 8.84

$J_{3,4}=7.3$; $J_{2,3}=5.0$
$J_{7,8}\approx7$

取代基	2	3	4	8	5	7	CH_3
2,4-Me_2		7.14					2-Me,2.70,4-Me,2.66
2,6-Me_2		7.21	7.90	7.90			2,2.72;6,2.50
6-OCH_3	8.71	7.28	7.97	7.97	7.00	7.35	—OCH_3,3.87
8-Me	8.72	7.12	7.82				3.77
5,7-Me_2	8.62	7.05	7.91	7.95			2.35,2.43
5,7-Cl_2	8.82	7.34	8.39	7.57			

三、吲哚衍生物的^{1}H-NMR 化学位移和偶合常数

表 4-63 部分吲哚衍生物的^{1}H-NMR 化学位移和偶合常数[48]



1	2	3	4	5	6	7	δ_2	δ_3	$\delta_{芳}$	其他 δ	J_{12}	J_{13}	J_{23}	J_{37}
H	H	H	H	H	H	H	6.68	6.38	6.90		2.4	2.1	3.3	0.7
H	CH_3	H	H	H	H	H		6.13	7.08	$\delta_{CH_3}=2.20$				
H	H	CH_3	H	H	H	H	6.80		7.18	$\delta_{CH_3}=2.30$				
H	H	H	CH_3	H	H	H	6.65	6.40			2.4	2.1	3.3	0.8
H	H	H	H	CH_3	H	H	6.58	6.24			2.4	2.0	3.2	0.6
H	H	H	H	H	CH_3	H	6.67	6.34			2.4	2.1	3.3	1.0
H	H	H	H	H	H	CH_3	6.67	6.31			2.3	2.15	3.3	
CH_3	H	H	H	H	H	H	6.82	6.48	7.17	$\delta_{NCH_3}=3.37$				
CH_3	Ph	H	H	H	H	H		6.53	7.17	$\delta_{NCH_3}=3.57$				
H	H	Ph	H	H	H	H	7.03		7.17					
H	CO_2Et	H	H	H	H	H		7.20						
H	H	CO_2Et	H	H	H	H	8.12							
H	H	$COCH_3$	H	H	H	H	8.34							
H	H	CO_2H	H	H	H	H	8.18							
H	CO_2H	H	H	H	H	H		7.20						
H	H	Br	H	H	H	H	7.04			$\delta_{2CH_3}=2.28$				
H	CH_3	H	H	CH_3	H	H		6.10		$\delta_{5CH_3}=2.40$				
										$\delta_{4H}=7.44$				
H	CH_3	H	H	Cl	H	H		6.10		$\delta_{6H}=7.02$				
										$\delta_{7H}=7.02$				

第九节 氨基酸的^{1}H-NMR 化学位移和偶合常数[67]

	δ	J	D_2O
$H_3N^+—CH_2COOH$ (b: H_3N^+; a: CH_2)	(a) 4.28 (b) 7.47	(a,b) 5.7	(a) 3.58
$H_3N^+—CH(CH_3)—COOH$ (a: CH; b: CH_3; c: H_3N^+)	(a) 4.49 (b) 1.86 (c) 7.41	(a,b) 7.3 (a,c) 5.8	(a) 3.79 (b) 1.49
$H_3N^+—CH(CH(CH_3)_2)—COOH$ (a: CH; b: CH; c: $(CH_3)_2$; d: H_3N^+)	(a) 4.32 (b) 2.60 (c) 1.25 (d) 7.33	(a,b) 4.2 (a,c) 5.7 (b,c) 6.9	

Structure	δ	J
$(CH_3)_2$ (e,f) — CH (d) — CH_2 (b,c) — H_3N^+(g)—CH(a)—COOH	(a) 4.48 (b), (c), (d) ≈2 (e) 1.11 (f) 1.10 (g) 7.38	(a,b), (a,c) ≈6.7 (a,g) 5.5 (d,e) 6.1 (d,f) 5.7
CH_3 (f) — CH_2 (d,e) — CH(b)—CH_3(c) — H_3N^+(g)—CH(a)—COOH	(a) 4.41 (b) 2.28 (c) 1.21 (d) 1.55 (e) 1.70 (f) 1.10 (g) 7.35	(a,b) 3.6 (a,g) 5.5 (b,c) 7.0 (b,d) 6.1 (b,e) 8.4 (d,e) 13.6 (d,f) 7.0 (e,f) 7.0
OH — CH_2 (b,c) — H_3N^+(d)—CH(a)—COOH	(a) 4.65 (b) 4.51 (c) 4.56 (d) 7.70	(a,b) 4.0 (a,c) 4.0 (a,d) 6 (b,c) 13.5
CH_3 (c) — CH(b)—OH — H_3N^+(d)—CH(a)—COOH	(a) 4.44 (b) 4.82 (c) 1.67 (d) 7.63	(a,b) 4.5 (a,d) 5.5 (b,c) 6.5
SH (d) — CH_2 (b,c) — H_3N^+(e)—CH(a)—COOH	(a) 4.68 (b) 3.36 (c) 3.41 (d) 1.84 (e) 7.58	(a,b), (a,c) 5.0 (a,e) 5.3 (b,c) 15.5 (b,d), (c,d) 9.1
S—CH_3 (e) — CH_2 (d) — CH_2 (b,c) — H_3N^+(f)—CH(a)—COOH	(a) 4.67 (b) 2.50 (c) 2.65 (d) 2.96 (e) 2.27 (f) 7.73	(a,b) 7.7 (a,c) 4.4 (a,f) 5.5 (b,c) 15.7 (b,d), (c,d) 6.5
Pyrrolidinium ring (N^+ with H h, H i), ring CH_2 d,e; b,c; f,g; CH a—COOH	(a) 4.78 (b) 2.74 (c) 2.50 (d) 2.35 (e) 2.29 (f) 3.82 (g) 3.76 (h) 8.08 (i) 7.71	(a,b) 9.0 (a,c) 7.0 (a,h) 6.6 (a,i) 4.4 (b,c) 14.0 (b,d), (b,e), (c,d), (c,e) ≈6.8
Pyrrolidinium ring with HO (d), ring CH_2 b,c; e,f; N^+ with H g, H h; CH a—COOH	(a) ≈5 (b) 2.95 (c) 2.56 (d) ≈5 (e), (f) 3.9* (g) 8.60 (h) 8.00	(a,b) 8.2 (a,c) 10.4 (b,c) 15.0 (b,d) <2 (c,d) 4.2
COOH — CH_2 (b) — H_3N^+(c)—CH(a)—COOH	(a) 4.76 (b) 3.55 (c) 7.73	(a,b) 4.7 (a,c) 5.1

Structure	δ	J
$HOOC-CH_2(d)-CH_2(b,c)-CH(a)(COOH)-N^+H_3(e)$	(a) 4.60 (b) 2.63 (c) 2.55 (d) 3.01 (e) 7.71	(a,b), (a,c) 5.6 (a,e) 5.5 (b,c) 15.5 (b,d), (c,d) 6.2
$N^+H_3(g)-CH_2(f)-CH_2(e)-CH_2(d)-CH_2(b,c)-CH(a)(COOH)-N^+H_3(h)$	(a) 4.52 (b) 2.35 (c) 2.26 (d) ≈1.8 (e) 2.00 (f) 3.38 (g) 6.97 (h) 7.60	(a,b), (a,c) 5.6 (a,h) 5.8 (b,c) ≈15 (b,d), (c,d) ≈6.0 (e,f) ≈6.0 (f,g) ≈6.0
$NH_2(h)-C(=N^+H_2(h))-NH(g)-CH_2(f)-CH_2(d,e)-CH_2(b,c)-CH(a)(COOH)-N^+H_3(i)$	(a) 4.46 (b) 2.34 (c) 2.25 (d) ≈2.08 (e) ≈2.00 (f) 3.43 (g) 6.50 (h) 6.19 (i) 7.60	(a,b), (a,c) 5.3 (a,i) 5.5 (b,c) ≈15 (b,d), (b,e), (c,d), (c,e) ≈6 (d,f), (e,f) 6.5 (f,g) 5.3
Indol-3-yl $-CH_2(b,c)-CH(a)(COOH)-NH_3^+(e)$; indole C2-H (d)	(a) 4.71 (b) 3.79 (c) 3.57 (d) 7.25 (e) 7.05	(a,b) 4.0 (a,c) 8.0 (b,c) 15.5
Imidazol-4-yl (c, d) $-CH_2(b)-CH(a)(COOH)-NH_3^+(e)$	(a) 4.91 (b) 3.87 (c) 7.66 (d) 8.73 (e) 7.82	(a,b) 6.4 (c,d) 1.4
C_6H_5 (d, e, f) $-CH_2(b,c)-CH(a)(COOH)-N^+H_3(g)$	(a) 4.68 (b) 3.64 (c) 3.37 (d) 7.3 (e), (f) 7.4~7.5 (g) 7.33	(a,b) 4.5 (a,c) 8.5 (b,c) 14.5
$HO-C_6H_4$ (d, e) $-CH_2(b,c)-CH(a)(COOH)-N^+H_3(f)$	(a) 4.64 (b) 3.60 (c) 3.34 (d) 7.27 (e) 7.03 (f) 7.4	(a,b) 4.5 (a,c) 8.5 (b,c) 15.0 (d,e) 8.5

第十节 常用溶剂氢核的化学位移

常用溶剂的化学位称 δ[66]如图 4-1 及图 4-2。

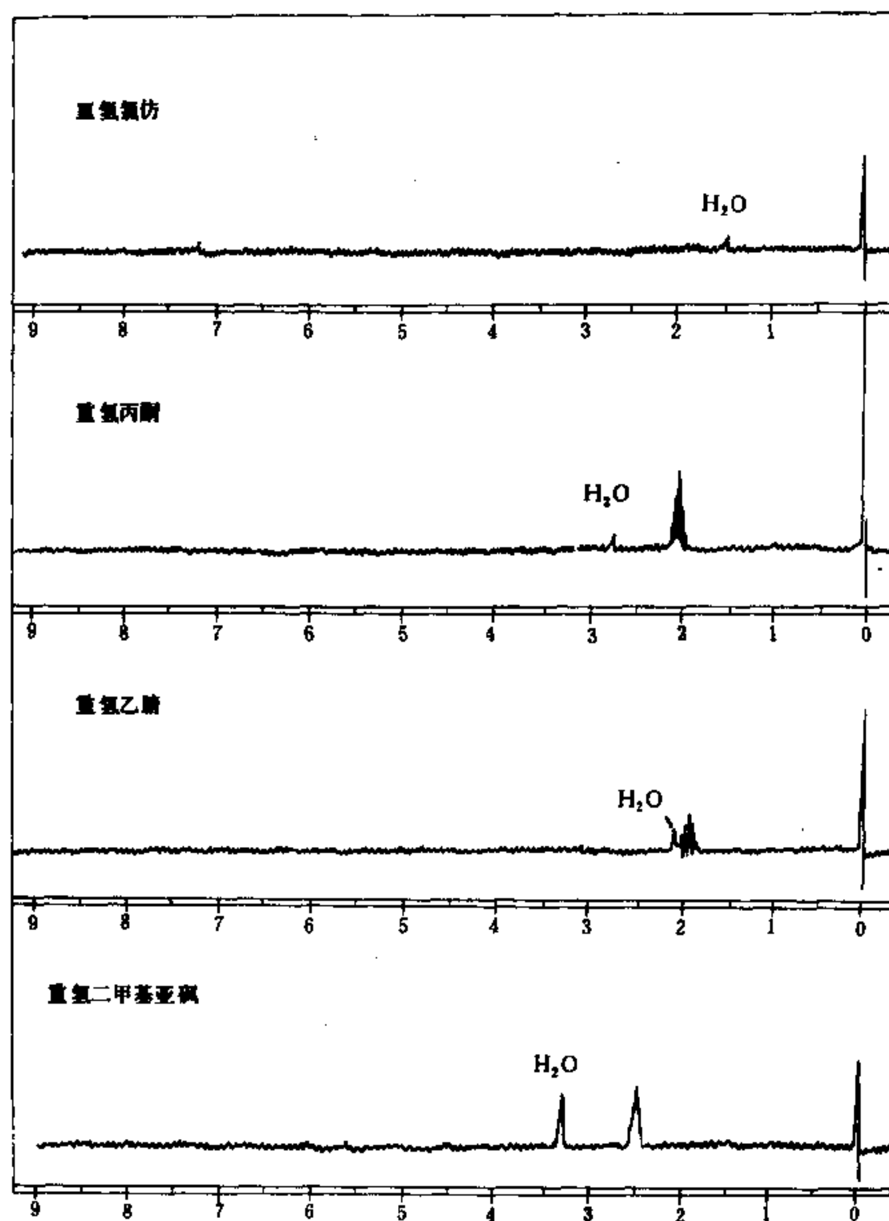


图 4-1 常用溶剂重氢氯仿、重氢丙酮、重氢乙腈及重氢二甲基亚砜的^{1}H-NMR 化学位移

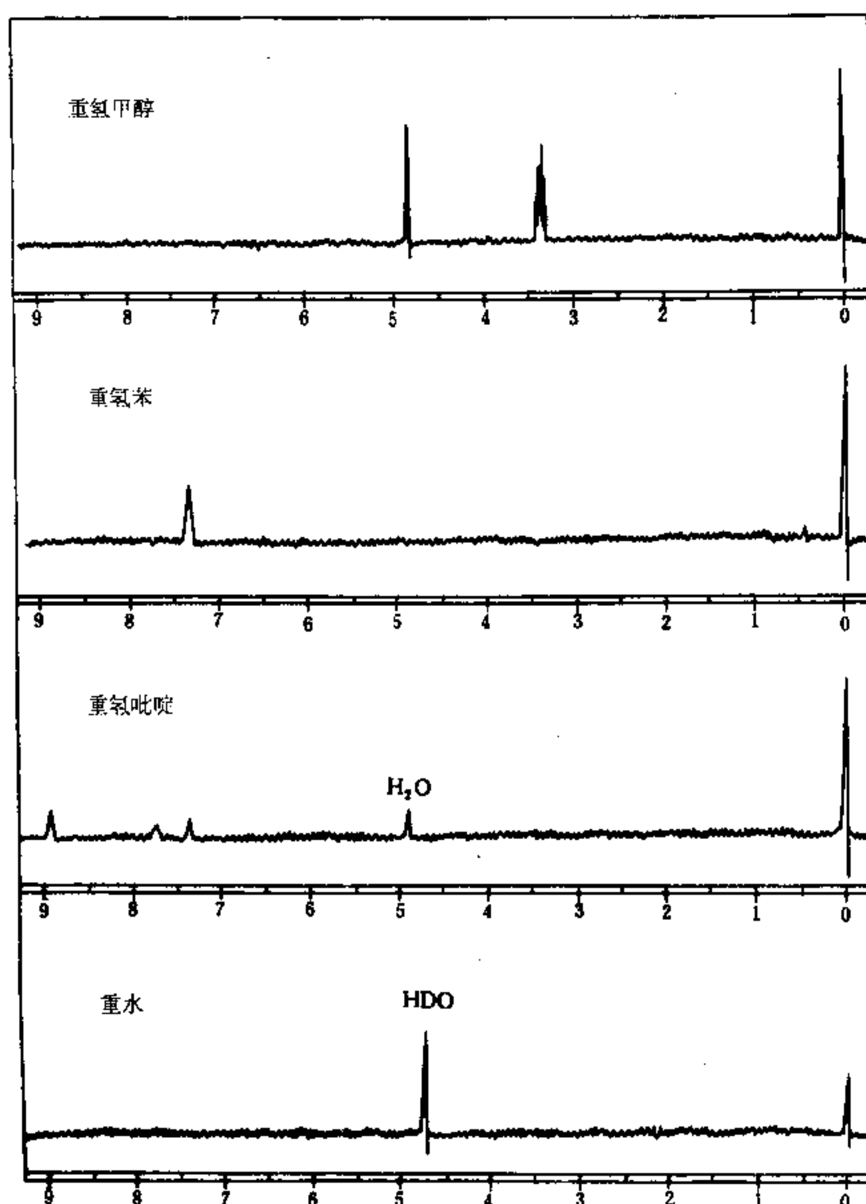


图 4-2 常用溶剂重氢甲醇、重氢苯、重氢吡啶及重水的^{1}H-NMR 化学位移

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第五章　质子核磁共振谱的偶合常数

第一节　同碳氢的偶合常数

表 5-1　无张力体系饱和碳上的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献
1	CH_4	±12.4	29, 30, 31
2		±12.2	17
3		−12.4	233
4		±12.8	100
5	CH_3CCl_3	±13.0	29～31
6		±13.0	98
7		±14.0	100
8		±14.06	5
9		±14.23	5
10		±14.9	274
11	—X: —CN	±12.6	279
	$—CO_2H$	±12.6	
	—ph	±12.7	
	—Cl	±13.2	
	—OH	±12.6	
	—OAc	±13.3	
12		−11.6～−15.0	285
13		−12.6	286
14		−17.0	280
15		−15.50	280
16		−13.0	281

续表

编号	化合物	$J_{同}$	文献
17		−12.5	282
18		A: −11.5 B: −13.8	283
19		A: −11.9	284
20		A: −10.0	284
21		A: −12.5 B: −13.5	281
22		−12.0	287
23		−11.0	288
24		−11.0～−11.9 −12.0～−12.9 −13.0～−13.9 −10.7 −14.0 −14.5 −15.0 −17.0	280
25		J_{56} = −15.6	289
26		J_{56} = −14.9～−15.0	289

表 5-2　连在固定取向的不饱和碳上的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献
1		−12.0	140
2		−15.5 −17.3	283
3		±15.8	128
4		±16.8	25
5		±17.1	200
6		±18.4	100
7		±18.5	179
8	—X —OH —Cl —Br	 ±18.2 ±19.1 ±19.8	31

续表

编号	化合物	$J_{同}$	文献
9		−21.5	29~31
10		−16	285
11		−17~−19	280
12		A: −16 ~ −20 C: −17 ~ −19.7	285
13		−10.4	285
14		A: −19.0	280
15		−9.8	285
16		A: −13.8 ~ −15.9	280
17	X = C或O	−16.0 −17.3, −17.4, −17.4, −18.0, −19.4, −18.0, −20.0(3例)	280
18		−17.0~−18.8	285
19		−17.5~−18.8	285
20		−15.3~−18.4	285
21		−18.5 −19.0(3例) −19.2	280
22		−15.0 −15.2 −15.5(4例)	280
23		−21.0	280
24		−16.4 −12.5, −12.6	280
25	X = O或N	−17.0 −18.5, −18.6 −19.0	280
26		−17.0~−18.9	285
27		−15.5	285
28		−17.5~−18.8	285
29		−17.7	285
30		−14.0(3例)	280

表 5-3 连在可自由旋转的不饱和碳上的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献
1	$(CH_3)_2CHC(OH)(CO_2H)CH_2CO_2H$	±12.7	198
2	CH_3NO_2	±13.2	29
3	$phCH_2CHXCO_2CH_3$	-13.56	110
4	$phCH_2CHXCO_2H$	-13.75	110
5	CH_2CO_2R	±14.0	56
6	CH_3	±14.4	29~31
7	N, CH_3	±14.5	37
8	$HO_2C—CH_3$	±14.6	29~31
9	$phCH_2CHN^+D_3CO_2H, Cl^-$	-14.6	118
10	$phCH_2CHND_2CO_2^-, Na^+$	-14.6	118
11	CH_3COCH_3	±14.9	29~31
12	$K^+, {}^-O_2CCH_2CHOHCO_2^-, K^+$	±15.3	8
13	$Na^+, {}^-O_2CCH_2CHND_2CO_2^-, Na^+$	-15.5	118
14	$HO_2CCH_2CHOHCO_2^-, K^+$	±16.4	8
15	$CH_3C\equiv N$	±16.9	29~31
16	$HO_2CCH_2CHOHCO_2H$	±17.1	8
17	$phCH_2C\equiv N$	±18.5	29~31
18	$N\equiv C—CH_2—CO_2CH_3$	±18.7	29~31
19	$N\equiv C—CH_2—CH=CH_2$	±19.4	29~31
20	$N\equiv C—CH_2—C\equiv N$	±20.4	29~31

表 5-4 直接连在氧或氮上并固定取向的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献
1	CH_3N, O, H, H, OH, OCH_3	±1.5	270
2	O, H, H, O, O, H, H	±1.5	178

续表

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
3		−8.3	111	12		A: −8.0 ~ −14.0	290
4		±8.5	227	13		A: −13.0 ~ −16.6	290
5	R R′: H H; H CH₃; CH₃ H	±9.0 ±9.0 ±9.0	23	14	AcO	A: −10.7 ~ −12.0	290
6		±9.6	117	15	OAc	A: −11.8 ~ −12.9	290
7		A: ±10.6 B: ±11.5	73	16		A: −5.8 ~ −6.3	285
8		±11.3	19	17		A: −16.0 ~ −20.0 D: −11.0 ~ −13.4	285
9		±11.8	224	18		D: −10.0 ~ −12.0	290
10		−12.50	5	19		A: −11.0 ~ −14.0	285
11		−12.69	5	20		A: −13.0	285
				21		A: −16.4 ~ −18.0 E: 11.0	285 290
				22		A: −8.0 ~ −11.2	285
				23		A: −8.0 ~ −10.0	285
				24		D: −12.5 ~ −13.0	290
				25		A: −17.0 ~ −18.0	290

续表

编号	化合物	$J_{同}$	文献
26		−8.8 ~ −10.5	285
27		−6, −6.7, −6.9 −7.0 ~ −8.0 (12 例) −8.1 ~ −9.0 (12 例) −9.5 −10.0 ~ −10.5 (6 例) −11.3	290
28		−11.8, −11.8	290
29		−11.0	290
30		−8.0, −8.5	290
31		−17.0	285
32		−3.4 ~ −7.0	290
33		−11.50	285
34		−8.6, −9.5, −9.5, −10.0 −10.2, −10.5, −11.0 −15.0	290
35		−11.50	290
36		−16.8 ~ −19.6 (6 例)	290
37		−9.65	290
38		−12.1 ~ −12.7 (4 例)	290
39		−16.5 ~ −19.6	290
40		−15.0	290
41		−15.0	290
42		−6.0(4 例) −6.25, −8.5, −9.0, −9.0	290
43		−0.7 ~ −5.0 (9 例)	290
44		−3.4 ~ 3.8 (5 例) −4.0 ~ −4.8 (11 例) −5.7, −5.9, −6.5 −8.0, −10.0	290
45		−13.0	290
46		−5.2, −5.2	290
47		−8.1, −9.8, −9.4	290
48		−8.5, −8.6	290
49	H^A H^B X Y	X Y −8 O CH_2 −0 O O −9.5 N CH_2 −3.5 N N −2.5 N O −10 S CH_2 −9.7 S S	290
50		−14.0	290

续表

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
51		-8.8 -9.0~-9.9 (6例) -10.0~-12.0 (15例)	290	57		-1.0	290
52		-17.0~-18.8	285	58		Ca.1 (2例)	290
53		-8.64	290	59		-5.4 (2例) -5.8 -6.0 (3例)	290
54		-13.0 (4例)	285	60		-7.5	290
55		-7.0~-9.0 (28例)	290				
56		-8.5~-9.79 (11例)	290	61		0.0~0.4 (J_2)	290

表 5-5 连在可自由旋转的其他元素上的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
1	CH_2Cl_2	±7.5	34	13	CH_3OH	-10.8	23, 34
2	CH_3I	±9.2	34	14	CH_3Cl	±10.8	34
3	$CH_3CH_2O—CHCH_3—OCH_2CH_3$	-9.3	171				
4	$BrCH_2—C(Br)(CO_2H)—CH_3$	±(9.68~10.04)	260	15		±11.0	84
5	CH_3F	±9.6	34				
6	$BrCH_2CHBrCH_3$	-9.8	104				
7	$BrCH_2CHBrCO_2H$	-10.0 -9.9	112 114				
8	CH_3Br	-9.9	195				
9	$CH_3CH_2O—SO—OCH_2CH_3$	±10.2 -10.45	40 171	16	$HOCH_2C(CH_3)_2CHOHCONH_2$	±11.0	117
10		±10.5	142	17	R: CH_3, X: H	±11.0	145
					R: CO_2CH_3, X: H	±11.0	
					R: CO_2CH_3, X: Ac	±11.0	
11	$CH_3CHOCH_3CH_2OSO_2Ph$	±10.6	79		R: CO_2OAc, X: Ac	±11.0 (±7.5?)	
12	$BrCH_2—C(Br)(CO_2CH_3)—CH_3$	±(10.65~10.98)	260		R: $=CH_2$, X: H	±10.8	

续表

编号	化合物	$J_{同}$	文献
18	$ClCH_2CHClCH_3$; H, OAc; $AcO\cdot H_2C$; R; R / H / CH_3	-11.1	104
19		±12.6 ±12.6	23
20	$O_2CCHND_2CH_2SSCH_2CHND_2CO_2^-$, $2Na^+$	-13.2	118
21	$HO_2CCH\overset{+}{N}D_3CH_2SSCH_2CH\overset{+}{N}D_3CO_2H$, $2Cl^-$	-15.1	118
22	$CH_2(CN)_2$	-20.3	291
23	$PhCH_2CN$	-18.5	291
24	CH_3CN	-16.9	291
25	CH_3—CO—CH_3	-14.9	291
26	CH_3—COOH	-14.5	291
27	$ArCH_3$	-13.8~-14.8	292
28	OAc; H_A—C—H_B; CHOAc; OH	J_{AB} = -12	293
29	OAc; H_A—C—H_B; C=O; OH	J_{AB} = -17.6	293
30	$CH_3CH(OCH_AH_BCH_3)_2$	J_{AB} = -9.4	294

表 5-6 具有张力环系的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献
1	X Y: H H H CH_2OH H Br H CO_2CH_3 H CH_2Br H CH_2OAc H $CON(CH_3)_2$ H COCl H $COCH_3$ H CO_2H HO H TosO H (=O) H OH H OAc H OTos Br H H CF_3CO_2	±5.4 ±6.0 ±6.0 ±6.3 ±6.6 ±6.6 ±6.6 ±6.6 ±6.6 ±6.6 ±6.8 ±7.1 ±7.2 ±7.6 ±7.8 ±7.8 ±8.1 ±8.4	278
2	Y: CO_2CH_3 COCl CO_2H	±6.4 ±6.6 ±6.6	278
3	Cl, F, F, Cl, Ph, CH_3, H, H	±13.7	265
4	X: CO_2H NH_2 Br	-4.30 -5.5 -5.85	213 158 213
5	X Y: (—CH_2—CH_2—) Ph CO_2H CH_3 CH_3 (—$CH_2CH_2CH_2$—) Ph Br Cl Cl	-3.9 -3.98 -4.5 -4.6 -5.9 -6.0	222 161 222 222 222 222
6	X Y Z: CO_2CH_3 CH_3 CO_2CH_3 CH_3 CH_3 CO_2H CH_3 CO_2CH_3 CO_2CH_3 CH_3 CH_3 Cl Cl Cl Ph Cl Cl OC_2H_5 Cl Cl OCH_3 Cl Cl O/2	-4.2 -4.3 -4.7 -5.98 -7.27 ±8.09 ±8.38 -8.7 -8.8	222 222 222 160 213 126 126 162

续表

编号	化合物	$J_{同}$	文献
7	W　X / Y　Z		
	CH_3　$CO_2CH_2CH_3$　CO_2CH_3	±4.2	222
	Cl　CO_2H　CH_3　CO_2H	±6.39	159
	CO_2H　Cl　CH_3　CO_2H	±6.44	159
	Cl　$CO_2CH_2CH_3$　CO_2CH_3	±6.52	159
	CH_3　CN　Cl　CO_2CH_3	±7.02	159
	CH_3　CN　CO_2CH_3Cl	±7.06	159
	Cl　Cl　Ph　CH_3	±7.10	126
8		±3.1	222
9		±4.2	179
10		±0.6	52
11		±2.0	208
12		+5.5	208, 254
13		+5.65 +5.66	238 96
14	X: −CN	+5.53	238
	X: −$COCH_3$	+5.78	
	X: −CO_2H	+6.28	
15		−10.0, −10.3	280
16		−10.0, −10.1	280
17		−8.0 ~ −12.0	285
18		−10.4 ~ −13.2	285
19		−10.5 ~ −11.5	285
20		−16.2 ~ −16.4	285
21		−10.0 ~ −12.0	285
22		−9.0, 9.8 −10.0 (2例) −11.2 (2例)	280
23		−7.5 −8.0 ~ −8.9 (12例) −9.0 (8例) −10.5 (5例) −11.0 (7例) −12.0 (3例)	280
24		ca.6.5 ca.5.0 ~ 6.0 −6.9 ~ −7.1 (7例)	280
25		−10.6 (2例) −11.8 (2例) −12.0 ~ −12.9 (18例) −13.0 ~ −13.8 (18例) −14.0	280
26		−9.0 −9.5 ~ −10.5 (4例)	280
27		−10.0	280

续表

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
28		-10.0, -10.5 -11.0 (2例) -11.5 (3例) -12.5	280	29		-8.0	280

表 5-7 其他结构形式的 CH_2 偶合常数

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
1		±16.8	269	10		A: -13.8~ -14.5	238p
2		±16.5	269	11		A: -11.1	238p
3	AcOCH₂ CH₂OAc	±12.6	205	12		A: -13.4~ -15.0	143
4	[X-C₆H₄-CH₂O]₂SO X: NO_2 ±12.81; Cl ±12.03; H ±11.87; CH_3 ±11.78; CH_3O ±11.57		219	13		A: -14.0	238p
				14		A: -13.9	143
5	PhCH₂OS(O)Ph	±11.37	219	15		A: -11.0	238p
6		-10.92, -15.31	249	16		-13.8	238p
7		±4.86	82	17		-11.5, -12.0	238p
8		|J| <0.4	211	18		-9.0~ -11.24 (13例)	238p
9		A: -12.6~ -13.0	238p	19		-11.5, -11.9 -12.0(2例)	238p

续表

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
20	O, S, H, H	-15.5	143	28	$H_2C=N(CH_3)_2$	±(10.3~12.0)	252
21	O, S, O, O, H, H	-14.0	143	29	$H_2C=N-N(R)-Ar$		
22	P, H, H	-Ca.15.5	238p		R　Ar		
23	A, S, N	18.5,19.0	238p		H　$O_2N-C_6H_4-$	±11.6	252
					CH_3　$O_2N-C_6H_4-$	±12.0	252
24	O, P, O, OPh	15.6	179		H　$O_2N-C_6H_3(NO_2)-$	±(11.0~11.4)	252
25	$H_2C=N-OH$	±(7.63~9.95)	251,252	30	$H_2C=N-R$		
26	$H_2C=N-OCH_3$	±(6.96~9.22)	251,252		R: t-Bu	±(16.11~16.52)	252
27	$H_2C=O$	+40.2~+42.42	253,288		t-Octyl	±(16.08~16.97)	252

第二节　邻位氢的偶合常数

一、饱和系统化合物的邻位氢偶合常数

表 5-8　连在饱和系统和取代烷类中 >CH—CH_3 的偶合常数

编号	化合物	$J_{邻}$	文献	编号	化合物	$J_{邻}$	文献
1	CH_3CH_3	+8.0	125,193		—Ru(CO)$_2$cp[①]	±7.69	82
2	CH_3CH_2X　X			2	—Fe(CO)$_2$cp	±7.63	82
					—ph	±7.62	94
	—MgBr	±8.96	109		—Mo(CO)$_3$cp	±7.61	82
	—Li	±8.90	109		—C≡N	±7.60	94
		±8.40	53		—PEt_2	±7.60	144
	—ZnEt	±8.6	216		—W(CO)$_3$cp	±7.54	82
	—Mn(CO)$_5$	±8.02	82		—CEt_3	±7.53	94,255
	—$SiEt_3$	±8.0	216			±7.3	
	—$SnEt_3$	±7.9	177		—CMe_2Et	±7.52	94
	—Re(CO)$_5$	±7.81	82		—(S)PEt_2	±7.5	144
	—$GeEt_3$	±7.8	216		—(Br)$_2PEt_2$	±7.5	144
	—$AsEt_2$	±7.8	199		—I	±7.45	94
	—$AsEt_3^+$	±7.8	199		—NEt_2	±7.4	199
	—$AsMeEt_2^+$	±7.8	199		—NEt_3^+	±7.4	199
	—(O)PEt_2	±7.75	144		—Br	±7.33	94

续表

编号	化 合 物	$J_{邻}$	文献
2	—PEt_3^+	±7.3	144
	—C(=O)—CH = CH_2	±7.32	94
	—CH_3	±7.26	276
	—$CORe(CO)_5$	±7.26	82
	—Cl	±7.23	94
	—$COMn(CO)_5$	±7.22	82
	—C≡CH	±7.2	216
	—NEt_2	±7.13	94
	—OAc	±7.12	94
	—OEt	±6.97	94
	—BEt_3^-	±6.8	199
	—OEt_2^+	±4.7	55
3	CH_3CHXCH_3　X		
	—CHO	±7.0	231,46
	—ph	±6.9	
	—I	±6.6	
	—Br	±6.5	
	—Cl	±6.4	
	—NHR	±6.3	
	—NH_2	±6.3	
	—OH	±6.2	
4	$HO_2C—CH(CH_3)—C(OH)(CH_3)—CH(CH_3)—CO_2H$	±7.2	248
5	$CH_3—CH(CH_3)—CH_3$	±6.8	273
6	H, O, CH_2, O, HCOH, CH_3, H, H, OH	±6.7,6.7	274
7	$CH_2CHBrCH_2Br$	+6.5	104
		+6.6	112
8	$CH_3—CH(OCH_3)CH_2OSO_2Ph$	±6.3	79
9	S, CH_3, H, H, H	+5.3	211
10	CH_3CHF_2	±4.5	107
11	H, CH_3, H, CH_3	±4.5	89

① cp—环戊二烯基。

表 5-9　六元环中 H—C—C—H 的偶合常数

编号	化 合 物	$J_{邻}$	文献
1	D, D, H, H, OX, D, OX, H X: -Ac; -H; -H; CH_3-C₆H₄-SO_2; $(CH_3)_2C<$	$J_{顺}$ $J_{反}$ ±3.6 ±7.1 ±3.8 ±7.1($CHCl_3$ 液) ±4.1 ±6.7(D_2O 液) ±2.7 ±7.8 ±5.4 ±5.4	189
2	D, D, H, H, D, OX, OX, H		

续表

编号	化合物	$J_{邻}$	文献
2	X: -Ac, -H, -H	$J_{顺}$ $J_{反}$ ±3.5 ±11.0 ±4.5 ±11.0($CHCl_3$) ±4.1 ±10.5(D_2O)	189
	CH_3—C_6H_4—SO_2	±3.6 ±7.9	
	$(CH_3)_2C<$	±3.5 ±11.0	
3	NHAc, OAc, OCH_3	$J_{1,2}$ $J_{2,3}$ ±9.1 ±9.1	20
4①	NHAc, OAc, OCH_3	±2.3 ±10.4	20
5①	NH_2, OH, OCH_3	±2.9 ±9.1	20
6①	NHAc, OAc, OAc	±2.8 ±10.7	20
7①	NHAc, OAc, OC_2H_5	$J_{1,2}$ $J_{1,3}$ ±8.8 ±8.8	20
8①	NHAc, OAc, OC_2H_5	±2.5 ±10.5	20
9①	NAc_2, OAc, OCH_3	±2.8 ±10.6	20
10①	NAc_2, OAc, OC_2H_5	±3.0 ±10.7	20
11	t-Bu, H, OH, H, H	$J_{顺}$ = ±4.31 $J_{反}$ = ±11.07	17
12	t-Bu, OH, H, H, H	$J_{顺}$ = $J_{反}$ ≈ ±3.0	17

续表

编号	化合物	$J_{邻}$	文献
13		$J=\pm2.1$	188
14		$J=\pm9.2$	188
15		$J_{顺}=+4.3$ $J_{反}=+12.4$	233
16	–X –F –Cl –Br –I	$J_{顺}$ ±1.2 ±2.4 ±2.8 ±4.3	212
17	–X –F –Cl –Br –I	$J_{反}$ ±10.4 ±11.4 ±11.8 ±11.9	212
18		$J_{顺}=\pm6.7$	241
19		$J_{12}=\pm8.2$ $J_{23}=\pm9.3$ $J_{34}=\pm9.3$ $J_{45}=\pm9.7$	190
20			124
21		$J_{4,5}=\pm8.1$	187

No. 20:

R^1	X	Y	J_{12}	J_{23}	J_{34}
CH_3	H	$CONH_2$	±2.3	±3.0	±10.0
C_2H_5	H	$CONH_2$	±2.2	±3.1	±9.8
CH_3	Ac	$CONH_2$	—	±3.1	±9.3
CH_3	$CONH_2$	H	±2.0	±3.3	±9.5
CH_3	$CONH_2$	Ac	±1.2	±3.2	±10.0
CH_3	H	H	±1.9	±3.2	—

续表

编号	化合物	$J_{邻}$	文献
22	AcO, AcO, AcO, H, H, O, O, OAc	$J_{4,5}=\pm4.2$	187
23	H, H, H, H, O, AcO, H, AcO, N, CH₃, CH₃, H, H (Ⅰ)		51
24	H, OAc, H, H, O, H, H		51

	(Ⅰ)	(Ⅱ)
$J_{1,2e}$	±4.0	±2.3
$J_{1,2a}$	±8.0	±2.3
$J_{2a,3}$	±12.0	±10.5
$J_{2e,3}$	±5.0	±6.0
$J_{3,4}$	±2.0	±2.0

表 5-10 不定构象开链化合物中 H—C—C—H 的偶合常数

编　号	化　合　物	$J_{邻}$	文　献
1	$CH_3-CHX-CHX-CH_3$	衍生物 / J_{23}: *meso* Br　7.8～8.8 *dl* Br　3.0～3.1 *meso* Cl　6.26～7.39 *dl* Cl　3.28～3.45 *meso* OAc　3.56 *dl* OAc　5.10 *meso* Ph　9.91 *dl* Ph　7.01	16,48
2	$BrCH_2-CHBr-CO_2H$	(+4.6, +10.9)	114
3	$Br-C(CH_3)(H)-C(H)(Br)-CO_2H$	10.7	115
4	$Br-CH_2-CHBr-CH_3$	4.01～4.20 10.82～9.76	104
		(4.2,10.6)	112
5	$Cl-CH_2-CHCl-CH_3$	(4.65,9.05)	106
6	$Cl_2CH-CHCl_2$	$J_{折} = \pm 2.01$ $J_{反} = \pm 16.35$	138,139
7	$Cl_2CH-CHF_2$	$J_{折} = \pm 2.01$ $J_{反} = \pm 10.25$	138,139
8	$Ph-CH_2-CHPhCO_2H$	(7.29,7.96)	110
9	$Ph-CH_2-CHPhCO_2CH_3$	(6.50,8.85)	110
10	$CH_3-CH(OCH_3)-CH_2OSO_2Ph$	(3.8,5.5)	79
11	$Ph-CH_2-CHNH_2CO_2H$	(5.5,7.7)HCl (5.1,7.9)NaOD	118
12	$(HO_2C-CHNH_2-CH_2-S)_2$	(3.7,8.2)HCl	118
13	$HO_2C-CH_2-CH(ND_3^+Cl^-)-CO_2H$	(5.3,5.3)	118
14	$Na^+\ ^-O_2C-CH_2-CH(ND_2)-CO_2^-Na^+$	(4.1,9.4)	118
15	$DO_2C-CH(ND_3^+Cl^-)-CH_2-SD$	(5.0,5.0)	118
16	$Na^+\ ^-O_2C-CH(ND_2)-CH_2-S^-$	(4.5,7.5)	118
17	*meso* $CH_3-C(OH)(H)-C(H)(H)-C(OH)(H)-CH_3$	(±6.2, ±6.9)	228

表 5-11　复杂环状化合物中H—C—C—H的偶合常数

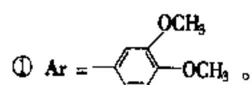
编号	化合物	$J_{邻}$	文献
1		$J_{顺}=3.2$ $J_{反}=13.5$	200
2[1]		J_{23} ±0.9　J_{34} ±4.3	69
3[1]		±9.5　±7.5	69
4[1]		±10.0　±3.3	69
5[1]		±1.0　—	69
6[2]		±8.9　±(6.9~7.0)	69
7[2]		±(10.0~10.3) ±(3.3~, 3.5)	69
8		$J_{顺}=±3.1$ $J_{反}=±12.9$	153
9		±2.8	146
10		±2.7	169

续表

编号	化合物	$J_{邻}$	文献
11		$J_{56}=\pm2.4$ $J_{57}=\pm1.8$ $J_{68}=\pm9.8$ $J_{78}=\pm3.6$	274
12		$J_{AA'}=12.3$ $J_{BB'}=3.2$ $J_{AB'}=4.0$	140
13		8.6	222
14	Y —OH —OAc —Cl —ph —CO_2H —CN	$J_{顺}$ $J_{反}$ ±7.4 ±2.4 ±7.6 ±2.5 ±8.0 ±3.2 ±8.9 ±4.2 ±8.5 ±4.4 ±9.3 ±4.6	279
15		$J_{19}=\pm6.0$ $J_{95}=\pm9.0$	7
16		±5.0	95
17	R H $O_2N-C_6H_4-CO-$	6.7 7.0	77
18		±(9.5~10.0)	267

续表

编号	化合物	$J_{邻}$	文献
19		$J_{顺}=\pm 11.1$ $J_{反}=\pm 6.0$	12
20		± 8.7	19
21		$\pm(2.7\sim3.8)$ (11 例, X, Y = C, O 取代基)	278
22		$J_{顺}=\pm(3.3\sim4.1)$ (5 例)	78
23		$J_{反}=\pm(2.1\sim2.7)$ (7 例)	78
24		立体化学 OH(2)OH(3) J_{23} J_{34} *exo* *exo* ± 7.7 ≈ 0 *exo* *endo* ± 2.3 ± 4.0 *endo* *exo* ± 2.2 ≈ 0 *endo* *endo* ± 8.9 ± 4.4	13
25		$J_{顺}=\pm 12.9$ $J_{反}=\pm 6.3$	186

① Ar =  。

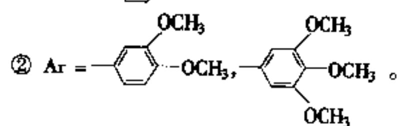
② Ar =  。

表 5-12　五元环中 H—C—C—H 的偶合常数

编号	化合物	$J_{邻}$	文献
1	R　立体化学	J_{23}	21
	-H　顺	±8.83	
	反	±8.85	
	-NO　顺	±8.72	
	反	±3.02	
	$-O_2S_{\varphi}$　顺	±8.61	
	反	±2.71	
2	顺	±7.00	21
	反	±5.09	
3		$J_{12}=\pm(3.5\sim3.8)$ $J_{23}\approx0.5$ $J_{34}=\pm(2.7\sim3.9)$ (13 衍生物)	3
4	R: H	J_{23} ±5.5; J_{34} <0.5	4
	R: $>C<{CH_3 \atop CH_3}$	J_{23} ±5.5; J_{34} <0.5	
5	G; R = H; R′ = H	J_{12} ±5.2	191
	G; R = Ac; R′ = Ac	±4.7	
	G; R = $>C<{CH_3 \atop CH_3}$; R′ = H	±2.9	
	G; R = H; R′ = H	±4.5	
	G; R = Ac; R′ = Ac	±3.8	
	G; R = $>C<{CH_3 \atop CH_3}$; R′ = H	±2.2	
	G; R = H; R′ = H	J_{12} ±5.1	191

续表

编号	化合物	$J_{邻}$	文献
7		$J_{12}=+3.9$ $J_{23}=+6.3$ $J_{34}=+1.6$	141
8		$J_{12}=0.0$ $J_{34}=0.0$	141
9		$J_{12}=0.0$ $J_{34}=0.0$	141
10		$J_{2,3a}=+7.66$ $J_{2,3b}=+10.44$ $J_{3a,4}=+1.41$ $J_{3b,4}=+4.31$ $J_{4,5a}=+1.22$ $J_{4,5b}=+4.09$	5
11		$J_{2,3a}=+10.48$ $J_{2,3b}=+3.84$ $J_{3a,4}=+4.71$ $J_{3b,4}=+2.09$ $J_{4,5a}=+4.57$ $J_{4,6b}=+0.94$	5
12		$J_{顺}=+5.85$	16
13		$J_{反}=+6.62$	16
14		$J_{顺}=+7.35$	16
15		$J_{反}=+7.20$	16
16	R^1 Ph, R^3 Ph, R^4 Ph, R^5 Ph	$J_{顺}$ ±10.4, $J_{反}$ ±5.5	143

续表

编号	化合物	$J_{邻}$	文献
16		$-\pm3.1$	
		$-\pm7.7$	
17		$J_{23}=2.5$ $J_{45}=2.5$	296
18		$J_{23}=1.2$ $J_{45}=1.2$	296
19		$J_{23}=8$ $J_{45}=8$	296
20		$J_{4,5}=6.3$	296
21		$J_{AA'}=J_{BB'}=7.1$(顺) $J_{AB'}=J_{A'B}=6.0$(反)	297
22		$J_{AA'}=5.85$ $J_{AX}=6.30$ $J_{AX'}=-0.25$	298
23		$J_{AA'}=8.35$ $J_{AX}=5.90$ $J_{AX'}=-0.15$	298
24		$J_{反}=6.62$	298
25		$J_{顺}=7.2$ 7.8	299

续表

编号	化合物	$J_{邻}$	文献
26		$J_{反}=7.7$ 7.8	299
27		$J_{顺}=7.2$ $J_{反}=4.6$	299
28		$J_{顺}=7.9$ $J_{反}=5.1$	299
29		$J_{顺}=8.0$	299
30	R R′ Me H Me Me *i*-Pr *i*-Pr *t*-Bu *t*-Bu	$J_{顺}$ $J_{反}$ 4.4 4.5 4.4 5.0 6.9 5.7 7.5 6.2	295
31		$J_{1,6}=7.6$ $J_{1,5}=6.1$ $J_{1,2}=4.5$	289
32		$J_{1,6}=7.6$ $J_{1,5}=2.8$ $J_{1,2}=4.7$	289
33		X J_{AB} $J_{AB'}$ CH_2 7.4 4.6 C=O 7.2 2.2 O 10.7 8.3 S 10.0 7.5	300
34		$J_{AA'}=6.80$ $J_{XX'}=0.0$ $J_{AX}=3.5$	301
35		$J_{AA'}=1.70$ $J_{XX'}=0.3$ $J_{AX}=2.6$	301

表 5-13　四元环中 H—C—C—H 的偶合常数

编号	化合物	$J_{邻}$	文献	编号	化合物	$J_{邻}$	文献
1		$J_{顺}=\pm6.3, \pm10.6$ $J_{反}=\pm5.9$	166	3		$(+10.0, +6.2)$	284
2		$J_{顺}=\pm6.1$ $J_{反}=\pm3.2$	42	4		$J_{顺}=\pm9.4$ $J_{反}=(+9.3, +4.5)$	192a
				5		$(+11.16, +7.67)$	249

表 5-14　三元环中 H—C—C—H 的偶合常数

编号	化合物	$J_{邻}$		文献
		$J_{顺}$	$J_{反}$	
1	—X: —Br	$J_{AB}=7.30$ $J_{BB'}=10.5$ $J_{CC'}=10.3$	$J_{AC}=3.92$ $J_{BC'}=6.6$ —	213
	—X: $—CO_2H$	$J_{AB}=8.0$ $J_{BB'}=10.5$ $J_{CC'}=11.0$	$J_{AC}=4.6$ $J_{BC'}=7.5$ —	213
	—X: $—NH_2$	$J_{AB}=\pm6.6$ $J_{BB'}=\pm12.5$ $J_{CC'}=\pm12.5$	$J_{AC}=\pm3.6$ $J_{BC'}=\pm7.5$ —	158
2	X: —Ph; Y: $—CO_2H$	—	6.95	161
	X: —Ph; Y: —Br	—	7.0	222
	X: —Cl; Y: —Cl	11.2	8.0	222
	X: $—CH_3$; Y: $—CH_3$	9.2	5.4	222
	$(—CH_2—CH_2—)$	8.9	5.2	222
	$(—CH_2CH_2CH_2—)$	9.7	6.3	222
3	X: CH_3; Y: CH_3; Z: Cl	7.39	4.11	160
	X: Cl; Y: Cl; Z: O/2	±7.8	±5.0	162
	X: Cl; Y: Cl; Z: O/2	±8.2	±4.8	162
	X: Cl; Y: Cl; Z: OC_2H_5	±8.25	±5.27	126
	X: Cl; Y: Cl; Z: OCH_3	±7.9	±5.28	126
	X: CH_3; Y: CH_3; Z: CO_2H	+8.0	+5.6	222
	X: CO_2CH_3; Y: CH_3; Z: CO_2CH_3	+8.6	+6.3	222
	X: CO_2H; Y: CO_2H; Z: CO_2H	±9.33	±6.55	126
	X: CH_3; Y: CO_2CH_3; Z: CO_2CH_3	+8.8	+6.6	222
	X: Cl; Y: Cl; Z: Ph	+10.5	+8.57	213
4		—	±5.61	126
5	X: $H_2C═CH—$; Y: CO_2R	±8.7	—	157
	X: Ph; Y: CO_2H	±9.1	—	222

续表

编号	化合物	X	Y	$J_{邻}$ $J_{顺}$	$J_{邻}$ $J_{反}$	文献
6	H_3C, CH_3; H, X; Y, H 环丙烷	$(CH_3O_2C)(H_3C)C{=}CH$—	$—CO_2CH_3$	—	±5.4	222
		$(HO_2C)(H_3C)C{=}CH$—	$—CO_2H$	—	±5.7	222
		$H_2C{=}CH$—	$—CO_2R$	—	±5.6	157
		$—CO_2CH_3$	$—CO_2CH_3$	—	±5.6	222
		—Ph	$—CO_2H$	—	±5.7	222
		—Ph	$—CONH_2$	—	±6.0	222
7	Cl, Cl; H, H; CH_3, Ph 环丙烷			±8.28	—	222
8	氮丙啶 (NH)			6.3	3.8	208
9	2-苯基氮丙啶 (NH, Ph)			6.0	±3.1	52
10	环氧乙烷			4.45	3.1	208
11	取代环氧乙烷 (X)	—Ph		4.06	2.52	96
		—Ph		4.04	2.49	238
		—CN		4.23	2.51	238
		$—CO_2H$		5.01	1.86	238
		$—CO_2CH_3$		5.21	1.95	238
12	环氧乙烷 (H, X; Y, H)	2-氯苯基 (Cl)	3,4-亚甲二氧基苯基	—	±1.9	196
		2-氯苯基 (Cl)	2-呋喃基	—	±2.18	196
13	硫杂环丙烷 (S)			7.15	±5.65	208
14	甲基硫杂环丙烷 (S, CH_3)			6.3	5.4	211

表 5-15 非环状化合物中 $H-\overset{|}{\underset{|}{C}}-CH=C\langle$ 的偶合常数

编号	化合物	Y	$J_{邻}$	文献
1	$H_2C=C(CH_3)H$		+6.40	47
2	$H_2C=C(CH_2-Y)H$	CH_3	6.22	47
		$n-C_3H_7$	6.55	47
		$i-C_3H_7$	7.00	49
		$i-C_4H_9$	7.46	49
		Cl	6.50	49
		Br	7.26	49
		I	7.68	49
		Ph	6.62	49
		F	5.33	285
3	$H_2C=C(CHY_2)H$	CH_3	6.41	49
		i-Bu	10.65	49
		Cl	7.04	286
		F	5.31	285
4	$(CH_3)_2C=C(H)-C(t\text{-Bu})(t\text{-Bu})-H$		±11.37	49
5	F(H)C=C(CH₃)H		7.0	33
6	H(F)C=C(CH₃)H		7.1	33
7	CH₃(H)C=C(H)CHO		6.9	131

表 5-16 环状化合物中 $H-\overset{|}{\underset{|}{C}}-CH=C\langle$ 的偶合常数

编号	化合物	环系 / X	$J_{邻}$	文献
1	H—C=C(H)—CH₂, (CH₂)ₙ	5	2.1	256
		6	3.1	
		7	5.7	
		8	7.8	
		9	8.2	
		10	7.8	
2	H H (+)		±1.6	80
3	H H, H		1.8	275
4	H H, H		2.02	97
5	H, X, H, H, S, O	H	2.8	134
		Br	3.1	
		CH_3	±3.0	
		CH_3O	±3.4	
6	H, H, H, H_3C, S, O		±2.6	134
7	CH_3O, CH_3O, CO_2O, H, NHAc, H, H, H, H, OH, OCH_3		±3.2	66
8	CH_3, H, H, X, (+)	H	±1.9	238
		SO_3H	±2.0	
9	H, H, H, O, O		±1.6	270
10	O, Br, H, H H		±4.2	45
11	H, Br, H, Br, H		±6.6	169

续表

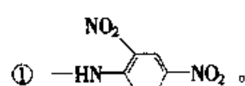
编号	化合物	$J_{邻}$	文献
12	R: =O H,OH	±2.3 ±1.8	60
13		J = ±2.2 J' = ±1.9	60
14		J = ±2.3 J' = ±3.5	60
15		±6.4	155
16	X: =O H,OH	±9.7 ±10.7	63
17		±0.8	65
18		±1.6	270

表 5-17 H—C—CH═X (X=O,N)体系的偶合常数

编号	化合物	$J_{邻}$	文献
1	$O{=}C(CH_3)H$	±2.83(+50℃) ±2.97(−100℃)	226
2	$O{=}C(CH_2CH_3)H$	±(0.8~1.3)	6
3	$O{=}C(CH(t\text{-}Bu)_2)H$	±5.0	49
4		±2.2	10
5	$O_2N—CH_2—CH{=}N—OH$	±6.0	54
6	$O_2N—CH_2—CH{=}N—OH$	±4.7	54

续表

编号	化合物	$J_{邻}$				文献
7	$O_2N-CH_2-C(H)=N-O^-$	±9.0				54
8	$O_2N-CH_2-C(H)=N-O^-$	±8.8				54
9	$CH_3-CH=N^+(O^-)_2$	±6.2				54
10	(1,4-二氢噌啉, 4-H,H; 3-H; 1-NH)	±3.6				36
		Y = ①	-HNPh	$-NHCH_3$	-OH	
11	$(H)(CH_3)C=N-Y$	±5.60	±5.75	±5.80	±5.80	172
12	$(H)(CH_3)C=N-Y$	±5.40	±5.55	±5.55	±6.20	172
13	$(H)((CH_3)_2CH)C=N-Y$	±7.60	±7.60	—	±7.6	172
14	$(H)((CH_3)_2CH)C=N-Y$	±4.9	±5.0	—	±6.3	172

① 

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表 5-18 丁二烯中 H—C=C—H 的偶合常数

编号	化合物	$J_{邻}$	文献
1	$H_2C=CH-CH=CH_2$	10.41	150
2	$CH_3O_2C-CH=CH-CH=CH-CO_2CH_3$	11.3	99
3	$CH_3O_2C-CH=CH-CH=CH-CO_2CH_3$	10.7	99
4	$HO_2C-CH=CH-CH=CH-CO_2H$	11.7	38
5	$Ph-CH=CH-CH=CH-Ph$	10.6	287

续表

编号	化合物	$J_{邻}$	文献	编号	化合物	$J_{邻}$	文献
6		11.5	28	9		11.24	287
7		12.5	28				
8		10.36	287	10		10.84	287

表 5-19 丙烯醛衍生物中 H—C=C—H 的偶合常数

编号	化合物	$J_{邻}$	文献	编号	化合物	$J_{邻}$	文献
1		7.81	31	4		7.7	245
2		7.7	39	5		7.73	287
3		7.9	131	6		7.95	287

表 5-20 炔类化合物的偶合常数

编号	化合物	$J_{邻}$	文献
1	H—C≡C—H	±9.53	193
		±9.8	125

二、直链双键化合物中邻位氢的偶合常数

表 5-21　乙烯衍生物中邻位氢及同碳氢的偶合常数

编号	化合物	$J_{顺}$	$J_{反}$	$J_{同}$	文献
1	$H_2C=CH_2$	+11.6	19.1	2.5	193
		11.4	18.8	2.0	236
		11.5	19.1	2.3	125
2	$H_2C=CH-$"MgBr"	17.2	22.1	7.4	109
3	$H_2C=CH-Li$	19.3	23.9	7.1	165
4	$(H_2C=CH)_4Si$	14.17	19.95	2.70	61,148
		15.33	20.47	4.38	
5	$(H_2C=CH)_3SiCH_3$	14.70	20.42	3.57	116
6	$(H_2C=CH)_nSiPh_{4-n}$	14.60	20.4	3.6	150
7	$(H_2C=CH)_4Ge$	13.32	20.07	2.93	63
8	$(H_2C=CH)_3P$	11.76	18.37	2.02	11
9	$(H_2C=CH)_4Sn$	14.1	20.3	2.8	206
10	$H_2C=CH-SCH_3$	10.3	16.4	-0.3	149
11	$H_2C=CH-SF_5$	9.8	16.6	±0.4	43
12	$H_2C=CH-SO_3H$	10.02	16.08	-1.40	22
13	$H_2C=CH-CO_2C_2H_5$	11.7	19.0	0.24	22
14	$H_2C=CH-CO_2H$	10.2	17.2	1.7	22
15	$H_2C=CH-COCH_3$	10.77	17.80	1.10	61
16	$H_2C=CH-COC_6H_5$	11.34	17.63	1.03	61

续表

编号	化合物	$J_{顺}$	$J_{反}$	$J_{同}$	文献
17	H, C≡N, H, H	11.75	17.92	0.91	148
18	H, Ph, H, H	11.48	18.59	1.08	259
19	H, H, H, O, OAc	10.6	17.5	1.0	203
20	H, H, H, O, O, OCH_3, OCH_3, CH_3O, O	10.2	17.9	1.0	281
21	H, CH_3, H, H	10.02	16.81	2.08	47
22	H, $C(CH_3)_2CONH_2$, H, H	10.64	17.47	0.97	242
23	H, CH_2F, H, H	10.66	17.21	1.54	285,286
24	H, CHF_2, H, H	10.85	17.47	0.67	285,286
25	H, CF_3, H, H	11.13	17.49	−0.15	285,286
26	H, CH_2Cl, H, H	10.11	16.92	1.27	49
27	H, $CHCl_2$, H, H	10.14	16.80	0.22	286
28	H, CCl_3, H, H	10.07	16.05	−0.42	62
29	H, CH_2Br, H, H	9.95	16.78	+1.22	49
30	H, CH_2I, H, H	9.69	16.49	1.25	49
31	H, CH_2Ph, H, H	10.05	17.00	1.96	49
32	H, OCH_3, H, H	6.0 6.6	14.1 14.4	−2.0 −2.2	149 102

续表

编号	化合物		$J_{顺}$	$J_{反}$	$J_{同}$	文献
33	$H_2C=CH-OC_2H_5$		7.0 6.9	14.5 14.9	-1.7 -1.7	149 102
34	$H_2C=CH-O\text{-}i\text{-}Bu$		6.9 6.3	14.4 14.2	1.8 -1.7	149 102
35	$H_2C=CH-OR$	R				
		t-Bu	6.2	13.2	-0.1	
		i-Pr	6.9	13.7	-1.2	
		(噻喃环)	5.7	14.7	-1.6	
		$-CH_2$-(呋喃基)	6.6	14.2	-1.9	102
		$-CH_2CH(C_2H_5)C_4H_9$	6.1	12.9	-1.8	
		n-Bu	6.9	14.4	-1.8	
		$ClCH_2CH_2-$	6.6	16.3	-2.7	
36	$H_2C=CH-OCHO$		6.3	13.8	-1.7	246
37	$H_2C=CHF$		4.65	12.75	-3.2	27
38	$H_2C=CHCl$		7.3	14.6	-1.4	27
39	$H_2C=CHBr$		7.1	15.2	-1.8	27

表 5-22 顺式二取代乙烯衍生物 H—C=C—H 的偶合常数

编号	化合物	$J_{顺}$	文献	编号	化合物	$J_{顺}$	文献
1	$CH_3CH=CHLi$	±17.4	250	7	$ClCH=CH-CH=CHCl$	+7.28	287
2	$EtO_2C-CH=CH-CO_2Et$	±11.9	210	8	$C_5H_{11}-CH=CH-OAc$	±7.0	239
3	$(CH_3CH=CH)_2Hg$	±11.1	209	9	$C_{16}H_{33}-CH=CH-OCH_3$	±6.4	271
4	$CO_2CH_3(CH_3)C=CH-CH=C(CH_3)CO_2CH_3$	±10.7	28	10	$ClCH=CHCl$	±5.2	210
5	$CH_3C_6H_4-S-CH=CH-CO_2C_2H_5$	±10.4	268	11	$FCH=CHCH_3$	±4.5	33
6	$CH_3C_6H_4-S-CH=CH-CO_2H$	±9.7	268	12	$FCH=CHBr$	±3.5	86
				13	$FCH=CHF$	-2.0	76,108

表 5-23　反式二取代乙烯衍生物 H—C=C—H 的偶合常数

编号	化合物	$J_{反}$	文献
1	CH_3, H / H, Li	±22.2	250
2	(CH_3, H / H)$_2$Hg	±19.2	209
3	CH_3, H / H, CO_2H	±14.9	182
4	CH_3, H / H, $CO_2C_2H_5$	±15.4	182
5	CH_3, H / H, CHO	±15.45	151
6	Ph, H / H, CH_3	±15.6	103
7	Ph, H / H, CH_2Cl	±14.8	85
8	Ph, H / H, CH_2OH	±15.0	85
9	CH_3O-C$_6$H$_4$, H / H, CH_3	±15.4	85
10	H, H, CO_2CH_3	±15.65	28
11	H, H, CO_2CH_3	±15.60	28
12	H, H, CO_2CH_3	±15.5	28
13	H, H, CO_2CH_3	±15.5	28

续表

编号	化合物	$J_{反}$	文献
14	H; H; CHO	±15.7	245
15	$C_2H_5O_2C$; H; H; $CO_2C_2H_5$	±15.5	210
16	CH_3; H; CH_3O_2C; CO_2CH_3; H; CH_3	±14.6	28
17	S; H; H; CO_2H	±15.4	268
18	S; H; H; $CO_2C_2H_5$	±14.9	268
19	CH_3O; CH_3O; H; H; NO_2	±14.0	270
20	Cl; H; H; Cl	±13.12	287
21	Cl; H; H; CH_2Cl	±13.1	207
22	n-$C_{10}H_{21}$; H; H; OCH_3	±12.5	271
23	n-C_5H_{11}; H; H; $OCOCH_3$	±12.5	239
24	Cl; H; H; Cl	±12.2	210
25	CH_3; H; H; F	±11.1	33
26	Br; H; H; F	±11.0	86
27	F; H; H; F	+9.5	108

表 5-24 1,1-二取代乙烯衍生物中端基同碳氢的偶合常数

编号	化合物	$J_{同}$	文献	编号	化合物	$J_{同}$	文献
1		±1.5	282	4		±(1.96~3.24) （与溶剂有关）	272
2		±3.5	264	5		±4.1	209
3		±3.0	264	6		±2.8	123

三、环状双键邻位氢的偶合常数

表 5-25 环烯中 H—C=C—H 的偶合常数

编号	化合物	$J_{邻}$	文献	编号	化合物	$J_{邻}$	文献
1	三元环物	|J|<2	183	8		±2.9	64
2	四元环物	±4.2	270	9		±3.7	64
3		±2.5	64	10		±2.9	64
4		±2.5	64	11	五元环物	±5.1 ±5.4	256 183
5		±2.8	64	12		±5.6 ±5.58	97 64
6		±2.7	64,83	13		+5.7	80
7		±2.8	64	14		+5.8	270
				15		+5.9	134

续表

编号	化合物	$J_{邻}$	文献
16	O, S	+6.0	134
17	CO_2CH_3	±6.0	64
18	CH_3O, Ph, OH	±5.6	64
19	CH_3O, O	±6.0	64
20	CH_3O, O	±6.3	64
21	CH_3OCO, O	±6.0	64
22	CH_3O, O	±6.0	64
23	CH_3O, O	±7.0	64
24	O, O	±5.9	93
25		±5.8	183
26		±5.05	183
27	X, Y; X = H, Y = OH	±6.0	175
	X = H, Y = OAc	±6.0	
	X = H, Y = CN	±6.0	
	X = AcO, Y = CN	±5.9	
28	O	|J| < 3	163
	六元环物		
29		±9.6	183
		±8.8	256
30	O	+10.2	25
31	O	±10.4	45
32	Ph, Ph, O	±10.3	64
33	O	±10.2	64
34	O	±10.2	64
35	Br, O, Ph, Ph	±9.8	45
36	Br, O	±9.9	45
37	Br, O, Ph, Ph	±9.7	45
38	$CHCl_2$, O	±10.0	64
39	$CHCl_2$	±10.5	64
40	CH_3O_2C, O	±10.5	64
41	CO_2H, O, $C{=}CH_2$, CO_2H, HO, H	±10.5	123
42	O	±10.3	64

续表

编号	化合物	$J_{邻}$	文献
43		±10.0	64
44		±10.0	64
45		±10.3	64
46		±9.9	64
47	CO_2CH_3	±10.0	64
48		±10.1	64
49	OH	±10.0	64
50	OCH_3, NCH_3	±10.1	220
51		±10.0	212
52	R, OCH_3, OCH_3		281
	R: H	±10.0	
	R: $H_2C=HC-C(CH_3)_2-$	±10.0	
53	HO, HO, CO_2CH_3	±8.6	164
	七元环物		
54		±10.8	256
55	CH_3O_2C	±10.3 (2X)	64
56	HO_2C	±10.0 (2X)	64
57	HO_2C	±9.9	64
58	CH_3O_2C	±9.7	64
59	N, $CO_2C_2H_5$	±10.1	155
60	CH_3O	±12.2	64
61	CH_3O	±12.5	64

续表

编号	化　合　物	$J_{邻}$	文献
62	OPh PhO	±12.3	67
63	OPh PhO	±13.0	67
	大环物		
64		+10.3	256
65		±11.8	15
66		±12.8	64
67		±12.6①	64
68		±10.7	256
69		+10.8	256
70		+15.1	256

① 共轭双键。

第三节　芳烃及其衍生物的偶合常数

一、取代苯衍生物的偶合常数

表 5-26　单取代苯衍生物的偶合常数

编号	化合物	偶合常数			文献
	$H^{B'}$ $H^{A'}$ H^{C} —X H^{B} H^{A}	$J_{邻}$ (J_{AB}) (J_{BC})	$J_{间}$ ($J_{AA'}$) ($J_{BB'}$) (J_{AC})	$J_{对}$ ($J_{AB'}$)	
1	—CPh_2Li	±7.9 ±6.6	— —	— —	243
2	—CH_2Li	±8.0 ±6.2	— —	— —	243
3	C(R)—Ph　R = H, CH_3	+8.2 +7.5	+1.2 +1.7 +1.2	+0.5	101
	R—ph	+7.7 +7.5	+1.2 +1.0 +1.2	+0.5	101
4	O, N	+7.90 +7.44	+1.73 +1.30 +1.34	+0.59	285
5	O, Ph	+7.81 +7.53	+1.78 +1.32 +1.29	+0.68	285

续表

编号	化合物	偶合常数			文献
	$H^{B'}$ $H^{A'}$ H^{C} —X H^{B} H^{A}	$J_{邻}$ (J_{AB}) (J_{BC})	$J_{间}$ ($J_{AA'}$) ($J_{BB'}$) (J_{AC})	$J_{对}$ ($J_{AB'}$)	
6	N	+7.91 +7.43	+1.94 +1.41 +1.26	+0.61	285
7	Ph, N, N, N, CH_3	+8.01 +7.43	+1.83 +1.37 +1.31	+0.59	285
8	$C\equiv CH$	+7.72 +7.61	+1.77 +1.37 +1.32	+0.64	285
9	$C\equiv C$	+7.80 +7.47	+1.79 +1.39 +1.27	+0.62	285

表 5-27 邻位取代苯衍生物的偶合常数

编号	化合物	偶合常数			文献
	H^{A} X H^{B} $H^{B'}$ $H^{A'}$ X	$J_{邻}$ (J_{AB}) ($J_{BB'}$)	$J_{间}$ ($J_{AB'}$)	$J_{对}$ ($J_{AA'}$)	
1	Cl, Cl	+7.9 +7.5	+1.7	+0.5	197
		+7.9 +7.7	+1.6	+0.5	88
		+8.1 +7.5	+1.5	+0.3	127
2	Br, Br	+8.17 +7.40	+1.61	+0.36	277
		+8.1 +7.3	+1.5	+0.3	197
3	I, I	+7.9 +7.3	+1.5	+0.3	197
4	OCH_3, OCH_3	+7.98 +7.53	+1.45	+0.4	127
5	COCl, COCl	+7.8 +7.6	+1.1	+0.6	197
6	CO_2CH_3, CO_2CH_3	+7.7 +7.43	+1.24	+0.6	127

续表

编号	化合物	偶合常数			文献
	H^A, X, H^B, $H^{B'}$, $H^{A'}$, X	$J_{邻}$ (J_{AB}) ($J_{BB'}$)	$J_{间}$ ($J_{AB'}$)	$J_{对}$ ($J_{AA'}$)	
7	NO_2, NO_2	+8.4 +8.0	+1.4	+0.1	88
8	H^A, CO_2CH_3, H^B, H^C, OH, H^D	J_{AB} = +7.98 J_{BC} = +7.20 J_{CD} = +8.37	J_{AC} = +1.78 J_{BD} = +1.15	J_{AD} = +0.43	113
9	H^A, NH_2, H^B, H^C, Br, H^D	J_{AB} = +7.6 J_{BC} = +7.0 J_{CD} = +7.9	J_{AC} = +1.7 J_{BD} = +1.7	J_{AD} = ±0.3	70

表 5-28 间位取代苯衍生物的偶合常数

编号	化合物	偶合常数			文献
	H^B, X, H^C, H^A, $H^{B'}$, X	$J_{邻}$ (J_{BC})	$J_{间}$ (J_{AB})	$J_{对}$ (J_{AC})	
1	NO_2, NO_2	+8.16 ±8.3	+2.07 ±2.2	+0.4 ±0.5	170 197
2	Br, Br	±8.1	±1.8	±0.4	197
3	I, I	±7.7	±1.6	±0.3	197
4	COCl, COCl	±7.9	±1.9	±0.6	197

表 5-29　对位取代苯衍生物的偶合常数

编号	化合物 $X-C_6H_4-Y$（H^A、H^B、$H^{A'}$、$H^{B'}$）	偶合常数 $J_{邻}$	$J_{间}$		$J_{对}$	文献
1	$H_2N-C_6H_4-OCH_3$	8.5	2.8	2.8	0.5	197
2	$H_2N-C_6H_4-Cl$	8.6 8.5	2.5 2.67	2.8	0.4 0.34	197 75
3	$H_2N-C_6H_4-Br$	8.5	2.3	2.9	0.3	197
4	$H_2N-C_6H_4-I$	8.5	2.9	2.2	0.3	197
5	$H_2N-C_6H_4-NO_2$	9.0	2.6	2.3	0.3	197
6	$CH_3O-C_6H_4-Cl$	8.8	2.5	3.1	0.3	197
7	$CH_3O-C_6H_4-Br$	8.7 8.75	2.5 2.55	3.1 3.0	0.3 0.3	197 113
8	$CH_3O-C_6H_4-I$	8.9	2.4	3.0	0.4	197
9	$CH_3O-C_6H_4-NO_2$	9.0 9.03	2.7 2.88	2.7	0.3 0.23	197 75
10	$Cl-C_6H_4-Br$	8.4 8.6 8.6	2.5 2.9 2.53	2.5 2.4 2.53	0.4 0.25 0.3	197 234 127
11	$Cl-C_6H_4-I$	8.4 8.4 ±8.31	2.4 2.7 ±2.38	2.4 2.2	0.4 0.3 ±0.31	197 234 75
12	$Cl-C_6H_4-NO_2$	8.7 ±8.65	2.2 2.49	2.8	0.3 0.29	197 75
13	$Cl-C_6H_4-C_6H_4-Cl$	±8.45	±2.4	±2.4	±0.3	127

续表

编号	化合物 $X-C_6H_4-Y$ (H^A, H^B, $H^{A'}$, $H^{B'}$)	偶合常数 $J_{邻}$	$J_{间}$		$J_{对}$	文献
14	$Cl-C_6H_4-OH$	±8.62	±2.80		±0.30	75
15	$Br-C_6H_4-I$	8.6 ±8.33	2.2 ±2.32	2.5	0.3 0.33	197 75
16	$Br-C_6H_4-NO_2$	8.9	2.2	2.6	0.4	197
17	$Br-C_6H_4-OH$	±8.56	±2.77		±0.36	75
18	$N\equiv C-C_6H_4-OCH_3$	8.8	2.2	2.7	0.4	197
19	$N\equiv C-C_6H_4-Cl$	8.4	2.1	2.1	0.9	197
20	$CH_3CO-C_6H_4-OCH_3$	8.7	2.3	2.6	0.4	197
21	$CH_3CO-C_6H_4-Cl$	8.4 ±8.18	2.2 ±2.23	2.2	0.5 0.43	197 75
22	$ClCO-C_6H_4-OCH_3$	8.9	2.4	2.7	0.3	197
23	$ClCO-C_6H_4-Cl$	8.4	2.3	2.3	0.5	197
24	$OHC-C_6H_4-OCH_3$	8.6	2.1	2.5	0.4	197
25	$OCH-C_6H_4-Cl$	8.3	2.1	2.1	0.4	197
26	$HO_2C-C_6H_4-OH$	±8.35	±2.38		0.29	75
27	$CH_3-C_6H_4-NH_2$	8.1	2.4	2.4	0.5	197

续表

编号	化合物 H^A H^B / X—⟨苯环⟩—Y / $H^{A'}$ $H^{B'}$	偶合常数 $J_{邻}$	$J_{间}$		$J_{对}$	文献
28	$CH_3-C_6H_4-OCH_3$	8.3	2.4	2.7	0.4	197
29	$CH_3-C_6H_4-Cl$	8.4 ±8.2 ±8.35	— ±2.3 ±2.2	— ±2.7	0.4 ±0.47 ±0.35	197 75 234
30	$CH_3-C_6H_4-Br$	8.1 ±8.08	2.3 ±2.15	2.3	0.6 0.4	197 75
31	$CH_3-C_6H_4-I$	7.9 ±7.8	2.0 ±2.07	2.4	0.6 ±0.42	197 75
32	$CH_3-C_6H_4-NO_2$	8.5	2.1	2.3	0.4	197
33	$(CH_3)_2CH-C_6H_4-OH$	±8.31	±2.45		±0.41	75

表 5-30 多取代苯衍生物的偶合常数

编号	化合物	偶合常数 $J_{邻}$	$J_{间}$	$J_{对}$	文献
1	H^A, H^B, H^C, NO_2, CH_3, Cl 取代苯	$J_{AB}=\pm8.0$ $J_{BC}=\pm8.0$	$J_{AC}=\pm2.3$	—	87
2	H^A, H^B, OCH_3, OH, OCH_3 取代苯	$J_{AB}=\pm8.8$	—	—	9
3	含 H^L, H^M, H^N, Cl 的苯并咪唑酮, N-取代 (H^A, H^B, H^C, Cl, Cl 苯基)	$J_{AB}=\pm8.7$ $J_{LM}=\pm8.9$	$J_{AC}=\pm2.3$ $J_{MN}=\pm2.0$	—	218

续表

编号	化合物	偶合常数			文献
		$J_{邻}$	$J_{间}$	$J_{对}$	
4	1-Cl-2,4-$(NO_2)_2$, H^B, H^A, H^C	$J_{AB}=\pm 8.7$	$J_{AC}=\pm 2.7$	$J_{BC}<0.3$	87
5	1-OH-2,4-$(NO_2)_2$, H^B, H^A, H^C	$J_{AB}=\pm 9.2$	$J_{AC}=\pm 2.9$	$J_{BC}<0.3$	87
6	1-OH-2-NO_2-4-Cl, H^B, H^A, H^C	$J_{AB}=\pm 9.0$	$J_{AC}=\pm 2.5$	$J_{BC}=\pm 0.48$	9
7	CH_3O, OH, OCH_3, OCH_3, H^C, H^A, H^B	$J_{AB}=\pm 8.7$	$J_{AC}=\pm 3.1$		224
8	1-F-2,4-$(NO_2)_2$, H^B, H^A, H^C	$J_{AB}=+9.4$	$J_{AC}=+3.0$	$J_{BC}=+0.1$	244
9	1,3,5-三甲基苯	—	±2.2	—	6a
10	1,3,5-Cl₃ (Cl, Cl, Cl)	—	±2.1	—	156
11	Br, Br, Br	—	±1.7	—	156
12	NO_2, NO_2, NO_2 (CH₃)	—	±1.9	—	156
13	OH, X, X, X; X: Br, Cl, NO_2	—	±2.3 ±2.5 ±2.8	—	156
14	OH, O_2N, NO_2, Cl	—	±2.8	—	156

续表

编号	化合物	偶合常数			文献
		$J_{邻}$	$J_{间}$	$J_{对}$	
15		—	±3.3	—	156
16		—	±2.0	—	9
17		—	±2.3	—	9
18		—	±2.4	—	9
19		—	±2.2	—	9
20		—	±2.0	—	9
21		—	±2.2	—	9
22		±9.0	—	—	281

二、其他芳环氢的偶合常数

表 5-31　部分其他芳环化合物的偶合常数

编号	化合物	$J_{邻}$	$J_{间}$	$J_{对}$	文献
1		$J_{AB}=\pm 8.1$ $J_{BB'}=\pm 6.4$	$J_{AB'}=\pm 1.1$		168

续表

编号	化合物	$J_{邻}$	$J_{间}$	$J_{对}$	文献
2		$J_{AB}=\pm 8.3$ $J_{BB'}=\pm 6.5$	$J_{AB'}=\pm 1.2$		168
3		$J_{AB}=\pm 7.6$	—	—	168
4		$J_{AB}=\pm 8.0$ $J_{BC}=\pm 7.3$	$J_{AC}=\pm 1.3$	—	168
5		$J_{AB}=\pm 8.3$ $J_{BB'}=\pm 6.5$	$J_{AB'}=\pm 1.2$		168
6	RO	$J_{AB}=\pm 8.5$	—	—	174
7		$J_{AB}=\pm 3.7$ $J_{CD}=\pm 11.5$	$J_{DE}=\pm 1.3$	—	35
8		$J_{AB}=\pm 3.9$	—	—	80
9		$J_{AB}=\pm 13.3$ $J_{BC}=\pm 8.0$	—	—	261
10		$J_{AC}=+8.4$ $J_{AB}=+7.3$ $J_{BD}=+8.4$	$J_{BC}=+1.6$ $J_{AD}=+1.6$	$J_{CD}=+0.5$	32

续表

编号	化合物	$J_{邻}$	$J_{间}$	$J_{对}$	文献
11	H^A, H^B, H^C, H^D	$J_{AC}=+8.6$ $J_{AB}=+6.9$ $J_{BD}=+8.6$	$J_{BC}=1.4$ $J_{AD}=1.4$	$J_{CD}=0.5$	32
12	H^A, H^B, H^C, H^D, O, O	$J_{AC}=+8.3$ $J_{AB}=+7.4$ $J_{BD}=+8.3$	$J_{BC}=1.4$ $J_{AD}=1.4$	$J_{CD}=0.5$	32

三、芳杂环氢的偶合常数

表 5-32 吡啶衍生物的偶合常数

编号	化合物	偶合常数			文献
		$J_{邻}$	$J_{间}$	$J_{对}$	
1	H^A, H^B, H^C, H^D, N, Cl	$J_{AB}=7.75$ $J_{BC}=7.22$ $J_{CD}=4.67$	$J_{AC}=0.96$ $J_{BD}=1.98$	$J_{AD}=0.75$	181
2	N, C≡N	$J_{AB}=7.63$ $J_{BC}=7.61$ $J_{CD}=4.64$	$J_{AC}=1.20$ $J_{BD}=1.73$	$J_{AD}=0.99$	181
3	N, Br	$J_{AB}=7.57$ $J_{BC}=7.02$ $J_{CD}=4.48$	$J_{AC}=1.13$ $J_{BD}=1.94$	$J_{AD}=0.76$	181
4	N, $COCH_3$	$J_{AB}=7.48$ $J_{BC}=8.02$ $J_{CD}=4.53$	$J_{AC}=0.31$ $J_{BD}=1.79$	$J_{AD}=0.84$	181
5	N, COPh	$J_{AB}=7.88$ $J_{BC}=7.58$ $J_{CD}=4.76$	$J_{AC}=1.24$ $J_{BD}=1.77$	$J_{AD}=0.93$	285
6	H^A, H^B, H^C, H^D, N, Cl	$J_{BC}=8.22$ $J_{CD}=4.69$	$J_{AD}=0.30$ $J_{BD}=1.52$	$J_{AC}=0.71$	281
7	N, Br	$J_{BC}=7.81$ $J_{CD}=4.76$	$J_{AD}=0.30$ $J_{BD}=1.44$	$J_{AC}=0.81$	181

续表

编号	化合物	偶合常数			文献
		$J_{邻}$	$J_{间}$	$J_{对}$	
8	(吡啶环，CHO，N)	$J_{BC}=7.85$ $J_{CD}=5.00$	$J_{AD}=0.0$ $J_{BD}=1.81$	$J_{AC}=0.88$	181
9	(吡啶环，$COCH_3$，N)	$J_{BC}=7.99$ $J_{CD}=4.87$	$J_{AD}=0.0$ $J_{BD}=1.79$	$J_{AC}=0.83$	181
10	(吡啶环，H^A，H^B，H^C，CH_3，N，NH_2)	$J_{AB}=7.2$ $J_{BC}=4.8$	$J_{AC}=1.7$	—	266
11	(吡啶环，H，Cl，Cl，H，N，F)	—	±2.45	—	105

表 5-33　呋喃衍生物的偶合常数

编号	化合物	X	J_{AB}	J_{BC}	J_{AC}	J_{AD}	文献
1	(呋喃环 A、B、C，—CH=CH—CHO)		1.81	3.41	0.75	—	245
			±1.83	±3.46	—	—	2
2	(X—呋喃—$CO_2C_2H_5$)	$—CH_3$	—	±3.3	—	—	258
		—Br	—	±3.4	—	—	
		$—CH_2Br$	—	±3.5	—	—	
		—Cl	—	±3.4	—	—	
		$—CH_2Cl$	—	±3.5	—	—	
3	(呋喃—X)	$—CO_2H$	±1.8	±3.5	±0.4	—	185
			±1.73	±3.51	±0.86	—	2
		—CHO	±1.8	±3.7	±0.8	—	185
			±1.65	±3.62	±0.82	—	2
		$—COCH_3$	±1.9	±3.7	±0.7	—	185
		$—CH_2NH_2$	±2.0	±3.3	±0.7	—	185
			±1.94	±3.18	±0.76	—	2
		$—CH_3$	±1.90	±3.12	±1.03	—	2
		$—CH_2SH$	±1.91	±3.25	±0.73	—	2
		$—CH_2OH$	±1.90	±3.17	±0.84	—	2
		$—CH=CHCO_2H$	±1.84	±3.44	—	—	2
		$—CONH_2$	±1.76	±3.57	±0.72	—	2
		$—CO_2Et$	±1.76	±3.47	±0.91	—	2
		$—COCH_2CO_2Et$	±1.72	±3.60	±0.82	—	2
		$—NO_2$	±1.92	±3.66	±0.98	—	2
		$—COCF_3$	±1.70	±3.70	±0.76	—	2
		—COCl	±1.70	±3.79	±0.79	—	2

续表

编号	化合物	J				文献
		J_{AB}	J_{BC}	J_{AC}	J_{AD}	
4	$ClCH_2$, CHO, O	—	±3.67	—	—	2
5	CO_2H, O	±1.8	—	±0.8	±1.5	2
6	CO_2H, CH_3, O	±1.94	—	—	—	2
7	CO_2H, CO_2H, O	±1.83	—	—	—	2
8	H_3C, CO_2H, O	—	—	—	±1.6	2

表 5-34 噻吩衍生物的偶合常数

编号	化合物 (H^B, H^C, H^A, S, H^D)	J				文献
		J_{AB}	J_{BC}	J_{AC}	J_{AD}	
1	S	4.7	3.35	1.0	2.85	113
2	S, CH_3	5.20	3.46	1.16	—	201
3	CH_3, S	4.88	—	1.28	2.94	201
4	CO_2CH_3, S, CHO	±5.1	—	—	—	129
5	CO_2H, S, CHO	±5.1	—	—	—	129
6	CH_2Br, S, NO_2	±5.1	—	—	—	265

续表

编号	化合物 (H^B, H^C, H^A, S, H^D)	J				文献
		J_{AB}	J_{BC}	J_{AC}	J_{AD}	
7	CHO, CO_2CH_3, S	±5.22	—	—	—	129
8	CHO, CO_2H, S	±5.24	—	—	—	129
9	NO_2, CH_2OH, S	±5.4	—	—	—	265
10	NO_2, CH_2Br, S	±5.5	—	—	—	265
11	CH_2SCN, NO_2, S	±5.5	—	—	—	265
12	I, I, S	±5.5	—	—	—	136
13	I, I, S, S	±5.5	—	—	—	136
14	Br, S, O, O	±5.25	—	—	—	129
15	I, I, S	—	—	±1.4	—	136
16	HO_2C, CHO, S	—	—	±1.4	—	129
17	OHC, CO_2H, S	—	—	±1.44	—	129
18	Br, S, O, O	—	—	±1.45	—	129
19	CH_3, CH_3, S	—	±3.46	—	—	201

续表

编号	化合物 (H^B, H^C, H^A, S, H^D)	R	J_{AB}	J_{BC}	J_{AC}	J_{AD}	文献
20	CH_3 S CHR_2	—Cl	—	±3.65	—	—	135
		—I		±3.60			
		—SCN		±3.60			
		—CN		±3.70			
		—CO_2CH_3		±3.65			
		—$COCH_3$		±3.70			
21	Br S O O		—	±3.7	—	—	129
22	I S CH_2SCN		—	±3.7	—	—	265
23	Br S CH_2OCH_3		—	±3.7	—	—	265
24	Cl S CH_2Cl		—	±3.7	—	—	265
25	Br S CH_2Cl		—	±3.7	—	—	265
26	Br S CH_2—NCS		—	±3.8	—	—	265
27	Br S CH_2OAc		—	±3.9	—	—	265
28	O_2N S CH_2OAc		—	±3.9	—	—	265
29	CH_3O_2C S CHO		—	±3.97	—	—	129
30	HO_2C S CHO		—	±4.0	—	—	129
31	O_2N S CH_2CN		—	±4.1	—	—	265

续表

编号	化合物	J				文献
		J_{AB}	J_{BC}	J_{AC}	J_{AD}	
32		—	±4.1	—	—	265
33		—	—	—	±3.5	129

表 5-35 吡咯衍生物的偶合常数

编号	化合物	J					文献
		J_{AB}	J_{BC}	J_{AC}	J_{AD}	J_X	
1		±2.5	±3.6	±1.4	—	—	221
2		±2.62	±3.74	±1.45	—	J_{AX} = ±2.70 J_{BX} = ±2.42 J_{CX} = ±1.45	
3		±2.68	±3.73	±1.36	—	J_{AX} = ±2.45 J_{BX} = ±2.26 J_{CX} = ±1.36	2

表 5-36 其他杂环化合物的偶合常数

编号	化合物	J	文献
1		J_{AB} = ±7.3	121

续表

编号	化合物	J	文献
2		$J_{AB}=\pm7.9$	121
3		$J_{AB}=\pm8.2$	121
4		$J_{AB}=\pm4.2$ $J_{CD}=\pm7.8$	44
5		$J_{AB}=\pm1.7$	202
6		$J_{AB}=\pm7.9$	59
7		$J_{AB}=\pm1.6$ $J_{AC}=\pm0.8$ $J_{BC}=\pm1.5$	237
8		$J_{AB}=\pm5.30$	122
9		$J_{AB}=\pm3.2$ $J_{AC}=\pm1.9$ $J_{BC}=<0.5$	24
10		$J_{AB}=\pm3.7$ $J_{AC}=\pm2.3$ $J_{BC}=\pm0.9$	24

续表

编号	化合物	J			文献
11		$J_{AB}=8.3$ $J_{BC}=6.6$ $J_{CD}=9.0$	$J_{AC}=1.4$ $J_{BD}=1.2$	$J_{AD}=0.6$ $J_{AX}=\pm 0.4$ $J_{DX}=\pm 0.9$	180
12		$J_{AB}=8.3$ $J_{BC}=7.0$ $J_{CD}=8.6$	$J_{AC}=1.4$ $J_{BD}=1.0$	$J_{AD}=0.4$ $J_{AX}=0.4$	180
13		$J_{AB}=7.6$ $J_{BD}=7.0$ $J_{CD}=8.0$	$J_{AC}=1.4$ $J_{BD}=1.4$	$J_{AD}=0.6$ $J_{AY}=0.8$	180
14		$J_{AB}=9.0$ $J_{BC}=6.0$ $J_{CD}=8.8$	$J_{AC}=1.2$ $J_{BD}=1.7$	$J_{AD}=0.4$	180
15		$J_{AB}=8.3$ $J_{BC}=4.2$	$J_{AC}=1.8$	$J_{AX}=0.9$	223
16		$J_{AB}=\pm 8.2$ $J_{BB'}=\pm 7.1$	$J_{AB'}=\pm 1.4$	$J_{AA'}=\pm 0.7$	40
17		$J_{AB}=\pm 8.6$ $J_{BB'}=\pm 7.2$	$J_{AB'}=\pm 0.8$	$J_{AA'}=\pm 1.0$	40
18		$J_{AB}=8.15$ $J_{BC}=6.89$ $J_{CD}=8.36$	$J_{AC}=0.95$ $J_{BD}=0.82$	$J_{AD}=1.04$	41

四、芳氢与侧链烷基氢的偶合常数

表 5-37 芳环与侧链的偶合常数(苄基偶合常数)

编号	化合物	$J^{邻}_{CH_3,H}$	$J^{对}_{CH_3,H}$	文献
1		-0.746±0.026	-0.619±0.016	302
2		-0.62±0.02		303
3		-0.7 ($J_{CH_3,H(2)}$)	-0.62±0.02	304
4		-0.7 ($J_{CH_3,H(1)}$)		
5			-0.75	305
6		-0.8		304
7		-1.1±0.1		303, 306, 307
8		-0.5		305
9		-0.5 ($J_{CH_3,H(3)}$)		305
10		-1.2		308
11		-1.2		
12			-0.7	305
13		-0.8		308
14		-1.0		
15		-1		309

续表

编号	化合物	$J^{邻}_{CH_3,H}$	$J^{对}_{CH_3,H}$	文献
16	CH_3	-1		
17	CH_3	-1.3		307
18	CH_3	-0.6		305
19	CH_3	-1.1		310
20	CH_3	-0.9		307
21	CH_2—CH_2	-0.9	-0.3	311
22	CH_2	-0.6		305
23	CH═C—CH_3	-1.5		312

五、稠环芳氢的偶合常数

表 5-38　多环芳香化合物的环间氢偶合常数

编号	化合物	取代基	J	文献
1	8 1 2 3 4 5 6 7	CH_3, NO_2 1-Cl-2-OH 1-Cl-2-OCH_3 1-Br-2-OH 1-Br-2-NH_2 1-NO_2-2-NH_2 1-Br-2-$NHCOCH_3$	$J_{4,5}\approx0.5$ $J_{4,5}=0.4$ $J_{4,8}=0.8$ $J_{4,5}=0.4$ $J_{4,8}=0.8$ $J_{4,5}=0.5$ $J_{4,8}=0.9$ $J_{4,5}=0.3$ $J_{4,8}=0.7$ $J_{4,5}=0.2$ $J_{4,8}=0.6$ $J_{4,5}=0.2$ $J_{4,8}=0.6$	313
2	8 9 1 2 3 4 10 5 6 7	9-取代	$J_{4,10}=0.4$ $J_{4,10}=0.8$	314 314

续表

编号	化 合 物	取 代 基	J	文献
3		1-OH 1-OCH_3 1,2,3,4-四氢- 9,10-Br 9,10-CH_3 9,10-CH_2CH_3 9-R 9-叔丁基 4-OCH_3	$J_{4,10}=0.7$ $J_{4,10}=0.6$ $J_{4,10}=0.7$ $J_{4,5}=0.3$ $J_{4,5}=0.3$ $J_{4,5}=0.3$ $J_{4,5}=0.4$ $J_{4,5}=0.4$ $J_{1,5}=0.8$ $J_{1,8}=0.8$	315 315 315 306 306 306 306 306 306 315
4		4-NH_2	$J_{1,5}=1.0$ $J_{1,8}=1.0$	315

第四节　远程偶合常数

一、芳香化合物的远程偶合常数

表 5-39　部分芳香化合物的远程偶合常数[316]

编号	化 合 物	J	编号	化 合 物	J
1		$J_{ao}=-0.6\sim-0.9$ $J_{am}=0\sim+0.3$ $J_{ap}\approx-0.6$	6		$J_{bc}=8.4$　$J_{be}=0.5$ $J_{bd}=1.5$　$J_{cd}=6.0$
2		$J_{ab}=0\sim0.8$	7		$J_{ab}=8.4$　$J_{bc}=7.2$ $J_{ac}=1.2$　$J_{bd}=1.3$ $J_{ad}=0.7$　$J_{cd}=8.1$
3		$J_{ab}=8.5$(衍生物:8~9) $J_{bc}=7.5$(衍生物:5~7) $J_{ac}=1.4$(衍生物:1~2) $J_{ad}=0.7$(衍生物:1) J_{ae}(衍生物:≈1)	8		$J_{ab}=7.5$　$J_{bc}=6.5$ $J_{ac}=1.6$　$J_{bd}=1.6$ $J_{ad}=0.2$　$J_{cd}=7.2$
4		$J_{ab}=0$　$J_{bc}=7$ $J_{ac}=0$　$J_{bd}=0.6$ $J_{ad}=0$　$J_{cd}=8$			
5		$J_{bc}=6.7$　$J_{ab}=1.5$ $J_{cd}=8.1$　$J_{ad}=0.5$ $J_{bd}=1.2$	9		$J_{ab}=2.0$　$J_{bc}=5.8$ $J_{ac}=2.0$　$J_{cd}=0.7$

二、芳杂环化合物的远程偶合常数

表 5-40 部分芳杂环化合物的远程偶合常数[316]

编号	化合物	J
1		$J_{23}=4.0\sim6.0$ $J_{34}=6.9\sim9.1$ $J_{24}=0\sim2.7$ $J_{35}=0.5\sim1.8$ $J_{26}=0\sim0.6$ $J_{25}=0\sim2.3$
2		$J_{45}=4\sim6$ $J_{46}=2.5$ $J_{24}=0\sim1$ $J_{25}=1\sim2$
3		$J_{34}=5.1$ $J_{45}=8.0\sim9.6$ $J_{35}=1.8$ $J_{36}=3.5$
4		$J_{23}=1.8\sim3$ $J_{26}=0\sim-0.5$ $J_{25}=1.3\sim1.8$
5		$J_{23}=1.3\sim2.0$ $J_{34}=3.1\sim3.8$ $J_{24}=0.4\sim1$ $J_{25}=1\sim2$
6		$J_{23}=4.9\sim6.2$ $J_{34}=3.4\sim5.0$ $J_{24}=1.2\sim1.7$ $J_{25}=3.2\sim3.7$
7		$J_{12}=1$ $J_{13}=2$ $J_{23}=2.6$ $J_{34}=3.4$ $J_{24}=1.1$ $J_{25}=2.2$
8		$J_{45}=3.2$ $J_{24}=<0.5$ $J_{25}=1.9$
9		$J_{45}=1.6$ J_{24}及 $J_{25}=0.8\sim1.5$
10		$J_{邻}=2.3\sim3.1$ $J_{间}=1.0\sim1.6$

编号	化合物	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,7}$
11					
	4-Me	2.4	2.1	3.3	0.8
	5-Me	2.4	2.0	3.2	0.6
	6-Me	2.4	2.1	3.3	1.0
	7-Me	2.3	2.15	3.3	—
	无取代	2.4	2.1	3.3	0.7
12					
	2-Me	—	—		1.0
	4-Me	—	—	2.15	0.8
	5-Me	—	—	2.2	0.8
	6-Me	—	—	2.2	1.0
13	CH_3	—	—	—	0.9

三、相隔 4 个键的远程偶合常数

表 5-41　相隔 1 个双键和 3 个单键的远程偶合常数（H—X═Y—Z—H）

编号	化合物	^4J	文献
1		$J_{CH_3,H_3}=0.6$	317
2		$J_{CH_3,H_2}=1.1$	318
3		$J_{CH_3,H_3}=1.0$	318
4		$J_{CH_2\text{-}3}=0.9\sim1.1$	319 320
5		$J_{CH_2\text{-}3}=0.79$	319
6		$J_{CH_3\text{-}5}=1.4$	319
7		$J_{CH_3,H_5}=2.0$	321
8		$J_{AB}=-0.9$	322
9		$J_{AB}=-1.5$	322
10		$J_{CH_3,CH}=1.5$	323
11		$J_{CH_3,CH}=1.5$	324
12		$J_{CH_3,CH}=1.6$	325
13		$J_{CH_3\cdot CH}=1.1$	325
14		$J_{CH_3\text{-}4}=1.5$	325
15		$J_{CH_3\text{-}2}=1.9$	326
16	X = H, F, OCH_3	$J_{AC}=-1.5$	327
17		$J_{AC}=-1.0$	327
18		$J_{AB}=-3.28$	328
19		$J_{H_2,H_4}=<0.5$	329
20		$J_{H_2,H_4}=1.5$	329
21		$J_{AB}\approx J_{CB}\approx0.1$	330

表 5-42　相隔 4 个单键的远程偶合常数(^4J)

编　号	化　合　物	^4J	文　献
1		$J_{AB} = -0.8 \sim -1.0$	331
2		$J_{AB} \neq J_{AC} = 1 \sim 3$	331
3		$J_{AX} = 0.63$Hz $J_{AB} = 1.48$, $J_{BX} = 1.25$	318
4		$J_{AB} = +7.4$Hz	332
5		1.0～1.2 1.0～1.4 1.35～1.8	333,334 335 336
6		1.0～1.6	334
7		3～4 1.7～2.6	337 334
8		1.0	338
9		0～1.0	339
10		2.0～3.1	339,340
11		5.8～6.4	341,342
12		6.7～8.1	343,344

续表

编号	化合物	^4J	文献
13		8	345
14		10	346
15		18	346
16		14	347
17		10	346
18		$J_{1e3e}=2.0$	348
19		$J_{24}=1.5$	329
20		$J_{24}=2.0$	348
21		$J_{24}=1.5$	329
22		$ee'=2.1$ $aa'=-0.3$	349

续表

编 号	化 合 物	^4J	文 献
23		ea = +0.4 e'a' = −0.8	349
24		J ee' = 1.7	333
25	X = Cl X = Br	J4e6e = 1.55 J4e6e = 1.25 J2e4a = 0.70 J4a6a = 0.9	350
26	X = Cl X = Br	J4a6a = 2.25 J4a6e = 0.6 J4a6a = 1.3	350
27	—	J ae = −0.65	351
28	—	J ae = −0.4	351
29		Jee' = 0.5 ~ 0.9	352
30	—	$J_{HH'(exo)}$ = +1.2 ($\phi \approx 180°$, $\phi' \approx 150°$)	351
31	—	J2e4e = 1.5, 1.0 J2e6a = 0.4 ~ 0.5 J4e6e = 2.50 J4e6a = 0.3 ~ 0.4	352, 353 352
32	>C-t-Bu >S = O	J1e5e = 2.5 J7e11e = 2.5 J5a11a = 1.90 J1e5e = 2.70 J7e11e = 2.25 J5a11a = 1.85	354
33	—	J6,11e = +0.5 ~ 0.7 ($\phi \approx 120°$, $\phi' \approx 180°$) J6'11e = −0.7 ~ 0.9 ($\phi \approx 120°$, $\phi' \approx 60°$)	355
34		J1,3 = −0.6 J1,4 = −0.4 J2,4 = −0.4	356
35	—	J2e6e = 1.4 J2a6a = 1.0	357
36	—	Jee' = 2.2	357

四、烯丙体系的偶合常数

表 5-43 链式烯丙体系的偶合常数

化合物			J		文献
$R^2(R^3)C{=}C(CH_3)R^4$			$J_{顺}$	$J_{反}$	
R^2	R^3	R^4			
CH_3	H	CHO	+1.0	—	358
CH_3	H	COOH	1.2	—	359
CH_3	H	$COOCH_3$	1.2	—	359
CH_3	H	H	≈1.2	—	
H	CH_3	H	—	≈1.2	
Br	CH_3	$COOCH_3$	—	1.6	
H	CH_3	COOH	—	1.5	359
H	CH_3	$COOCH_3$	—	1.5	359
C_6H_5	CH_3	$COOCH_3$	—	1.0	360

表 5-44 反式和顺式烯丙体系的偶合常数

编号	化合物	平面夹角/(°)	^4J	文献
	反式物			
1		180	+1.3	361
2		160	+0.5	362
3		160	+0.95	362
4		120	2.2	361
5		120	−1.98	363
6		120	−2.1	364
7		120	1.3	361
8		120	−1.6	365
9		100	2.3	361
10		100	2.1	361
11		100	2.1	361
12		60	−1.94	366
13		20	0.7~0.8	361

续表

编号	化合物	平面夹角/(°)	^4J	文献
14	H(H)C=C(H)CH(t-Bu)$_2$	0	−0.1	361, 367
15	H, CH$_3$, H, N, H	0	0.4	368
16	顺式物 CH$_3$, H, N, H	60	1.6~2.0	368
17	H, H, C=, H$_2$, O, O	60	−1.36	366
18	H(H)C=C(H)CH(t-Bu)$_2$	0	−0.63	361, 367

五、相隔5个键的远程偶合常数

表 5-45 相隔5个单键的远程偶合常数

编号	化合物	^5J	文献
1	H$_A$—C(=O)—O—C(H)—C(H$_C$)—	$J_{AC}=0.4\sim0.6$	331 318
2	(A)CH$_3$, O, O, H, H	$J_{AB}=0.9$	369
3	$_A$H, H, H$_B$, H	$J_{AB}=2.3$	370
4	H$_B$, H$_C$, O, N, NH, H$_A$, CH$_3$	$J_{AB}=1.2$ $J_{AC}=1.8$	371
5	2, O, CH$_3$, O, 5	$J_{2e5e}=0.55$	372

表 5-46 相隔1个双键和4个单键的远程偶合常数（H—X═Y—Z—Q—H）

编号	化合物	^5J	文献
1	H—Y, X, H X = C,N Y = C = C,C = O,O,N	$J=0.1\sim1.0$	331 372
2	O, H, H, X X = O,S,NH	$J=0.1\sim1.0$	331 372
3	4, 3, O, CH$_3$	$J_{CH_3,4}=0.4$	319 320
4	H, O, H$_B$, O, H$_A$, H	$J_{AB}=1.6$	366
5	CH$_3$, S, O	$J_{CH_3,CH_2}=1.9$	323

续表

编号	化合物	^5J	文献
6		$J_{CH_3\text{-}CH_2}=2.5$	324
7		$J_{CH_3\text{-}CH_2}=2.7$	325
8		$J_{25}=3$	373
9		[illegible]	[illegible]

编号	化合物	^5J	文献
16		$J_{(CH_3)4\text{-}6}\leqslant 0.5$ R = —H，—OH，—OAc	318 376
17	X = CH，N	$J_{AB}=(+?)5.5\sim(+?)11$	331 377
18		$J_{AB}=0.4\sim 7.0$	331 378

表 5-47 相隔 2 个双键和 3 个单键的远程偶合常数

编号	化合物	^5J	文献
1		$J_{AB}=0.7$	379
2		$J_{AB}=0.6$ $J_{AC}=1.9$ $J_{AD}=2.9$	380
3		$J_{AB}\approx0.5$	381

六、相隔 6 个键的远程偶合常数

表 5-48 相隔 6 个单键的远程偶合常数

编号	化合物	^6J	文献
1		$J=1$	372

表 5-49 相隔 5 个单键和 1 个双键(或 2 个双键)的远程偶合常数

编号	化合物	^6J 或 ^7J	文献
1		$J_{H_9a,H_{12}a}=3.5$ $J_{H_9a,H_{12}e}=2.9$	382
2		$J_{H_9e,H_{12}a}=2.0$ $J_{H_9e,H_{12}e}<1$	382
3		$J_{CH_3,CH_3}=1$	383
4		$J_{CH_3,CH_3}=1$	383
5		$J_{CH_3,CH_3}=0.7$	384

七、其他类型的远程偶合常数

表 5-50 炔类、叠烯和其他共轭不饱和碳氢化合物的远程偶合常数

编号	化合物	J	文献
1	$H_3C-C\equiv C-H$	2.93	
2	$X-CH_2-C\equiv C-H$, X=Cl, Br, I	2.6~2.8	331
3	$H_3C-C\equiv C-CH_3$	2.7	
4	$H-C\equiv C-C\equiv C-H$	2.2	385
5	$H_3C-C\equiv C-C\equiv C-H$	1.27	
6	$H_3C-C\equiv C-C\equiv C-CH_3$	1.3	
7	$H_3C-C\equiv C-C\equiv C-C\equiv C-CH_2-OH$	0.4(J_{CH_3,CH_2})	
8	$R-CH=C=CH-R$	-5.8~-6.3	
9	$(CH_3)_2C=C=CH_2$	3.03	
10	(⬠, A)$=C=CH_{(B)}-C=CH_{2(B)}$	4.58(J_{AB})	
11	$_XH$>C=C=C=C<(H_B)(H_A)	$J_{AX}\neq J_{BX}\approx 1\sim 9$(?)	
12	$_XH$>C=C=C=C<($CH_{3(A)}$)($CH_{3(B)}$)	$J_{AX}\neq J_{BX}\approx 1$	
13	$H-C\equiv C-CH_2OH$	2.4	386
14	$H-C\equiv C-CH_2CH_3$	-2.4	387
15	$CH_3-C\equiv C-CH_2OH$	2.4	386
16	$CH_3-C\equiv C-CH_2Cl$	2.5	386
17	$CH_3-C\equiv C-CH_2CH_3$	2.55	388
18	$CH_3CH_2-C\equiv C-CH_2CH_3$	2.0	389
19	$CH_3-C\equiv C-C\equiv C-CH_2OH$	1.1	386
20	$H_AC\equiv CCH_B=CH_2$	-2.17	390
21	反—$CH_{2A}=CHCH=CH_{2B}$	1.30(反-反)	391
22	H_A—⬡—H_B	0.60(反-顺) 0.69(顺-顺) 1.11	392
23	$CH_{2A}=CHC\equiv CH_B$	0.8~0.9	390, 393
24	$CH\equiv CC\equiv CH$	|2.2|	394
25	$CH_{2A}=C(CH_3)C(CH_3)=CH_{2B}$	≈|1.0|	395
26	$CH_{2A}=C(CH_3)C\equiv CH_B$	0.28	396
27	$C_2H=CHCH=CHCH_3$	≈|0.6|	395

表 5-51 二茂铁类(Ferrocenes)衍生物的偶合常数

编号	化合物	^3J	^4J	文献
1		±2.5	—	240
2		—	±1.5	240
3	$COCH_3$	—	±1.4	240
4	H^A, H^B, H^C, O	J_{BC} = ±2.4	J_{AB} = J_{AC} = ±1.5	240
5	O, H, H	±2.5	—	240
6	$COCH_3$	—	±1.7	240
7	H^A, $COCH_3$, $COCH_3$, H^B, H^C	J_{BC} = ±2.40	J_{AC} = ±1.59	240
8	O	—	±1.5, ±1.5	240
9	$COCH_3$	—	±1.35	240

第五节 活泼氢的偶合常数

表 5-52 HOH 和 H—C—OH 系统的偶合常数

编号	化合物	J	文献
1	H—O—H	±7.2	152
2	CF_3—C(OH)(H)—O—C(OH)(H)—CF_3	±8.5	194
3	Cl_3C—C(OH)(H)—OH	±6.65	194
4	H, HO, O	±11.7	120
5	CH_3OH	±5.08, ±5.2	176
6	CH_3CH_2OH	±5.08	1
7	$CH_3CH_2CH_2OH$	±5.1	1
8	$CH_3CH_2CH_2CH_2OH$	±5.1	1
9	$(CH_3)_2CHOH$	±4.62	1
10	$HOCH_2$—C(NO_2)(CH_3)—C(H^A)(H^B)—OH^C	J_{AC} = +5.96 J_{BC} = +5.80	154

表 5-53 H—C—NH 系统的偶合常数

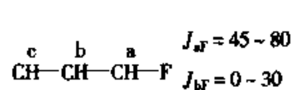
编号	化合物	J	文献
1	$(CH_3)_3N^+H$	±5.15	137
2	O=(环己烯酮)—NHCH₂Ph	±5.3	92
3	O=C(H^B)—N(H^A)—CH$_3$(C)	J_{AB} = ±1.8 J_{AC} = ±4.9	229
4	咪唑鎓（H, H^{A}N, NH^A, H^B, H^C）	J_{AB} = ±2.7 J_{AC} = ±1.9	262
5	2-甲基咪唑鎓（CH$_3$, H^{A}N, NH, H^B, H^C）	J_{AB} = ±2.6 J_{AC} = ±2.0	262

表 5-54 其他金属化合物的偶合常数

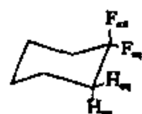
编号	化合物	J	文献
1	CH_3SnH_3	±2.70	106
2	$(CH_3)_2SnH_2$	±2.55 ±2.65	106 68
3	$(CH_3)_3SnH$	±2.37	106
4	$(CH_3)_2Sn(H)CF_2CF_2H$	±2.25	68
5	H_3SiPH_2	±5.1	90
6	H_3SiAsH_2	±5.1	90
7	H_3GePH_2	±4.8	90
8	H_3GeAsH_2	±4.8	90
9	B_2H_6（H, B, H, H, B, H 桥键结构）	±7.0	119

第六节 氢氟和氢磷的偶合常数[397]

一、氢氟间的偶合常数



$\overset{c}{CH}—\overset{b}{CH}—\overset{a}{CH}—F$ $J_{aF}=45\sim80$ （与构象有关：45～50） $J_{bF}=0\sim30$ （邻位交叉式：0～5） （对位交叉式：10～25） $J_{cF}=0\sim4$

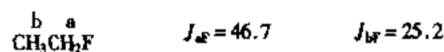


$J_{F_{ax}H_{ax}}=34$ $J_{F_{eq}H_{eq}}<8$

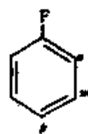
$J_{F_{ax}H_{eq}}=12$ $J_{F_{eq}H_{ax}}<8$



CH_3F $J=81$



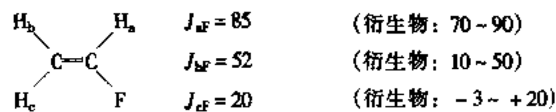
$\overset{b}{CH_3}\overset{a}{CH_2}F$ $J_{aF}=46.7$ $J_{bF}=25.2$



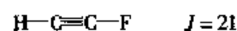
$J_{oF}=9.0$ （衍生物：6～10）

$J_{mF}=5.7$ （衍生物：4～8）

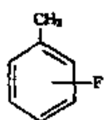
$J_{pF}=0.2$ （衍生物：0～3）



$H_b(H_c)C{=}C(H_a)F$ $J_{aF}=85$ （衍生物：70～90） $J_{bF}=52$ （衍生物：10～50） $J_{cF}=20$ （衍生物：-3～+20）



H—C≡C—F $J=21$



$J_o=2.5$

$J_m=0.0$

$J_p=1.5$

二、氢磷间的偶合常数

化合物	偶合常数	化合物	偶合常数
>P—H	$J=180\sim200$	$(CH_3CH_2O)_2P(=O)H^a$	$J_{aP}=630$
$(\overset{a}{C}H_3\overset{b}{C}H_2)_3P$	$J_{aP}=13.7$, $J_{bP}=0.5$	$[(CH_3)_2N]_3P$	$J=8.8$
$(\overset{a}{C}H_3\overset{b}{C}H_2)_4P^+$	$J_{aP}=18.0$, $J_{bP}=13.0$	$[(CH_3)_2N]_3PO$	$J=9.5$
$(\overset{a}{C}H_3\overset{b}{C}H_2)_3P=O$	$J_{aP}=16.3$, $J_{bP}=11.9$	$H^b(H^c)C=C(H^a)P$	$J_{aP}=10\sim40$, $J_{bP}=30\sim60$, $J_{cP}=10\sim30$
$(\overset{a}{C}H_3\overset{b}{C}H_2O)_3P=O$	$J_{aP}=0.8$, $J_{bP}=8.4$	$H^b(H^c)C=C(H^a)O—P$	$J_{aP}\approx7$, $J_{bP}\approx3$, $J_{cP}\approx1$
$(CH_3O)_2P(=O)C_6H_5$ (o, m, p)	$J_{oP}=13.3$, $J_{mP}=4.1$, $J_{pP}=1.2$		

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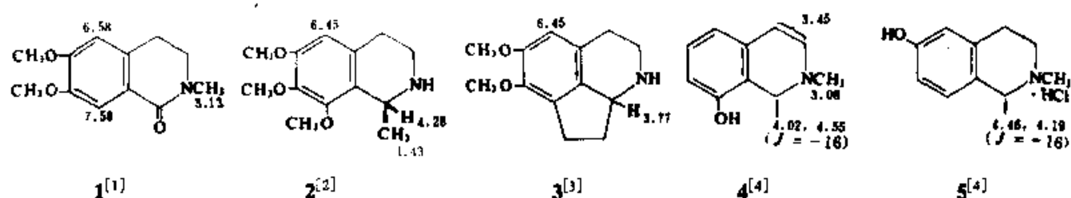
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第六章　生物碱的^{1}H-NMR 化学位移和偶合常数

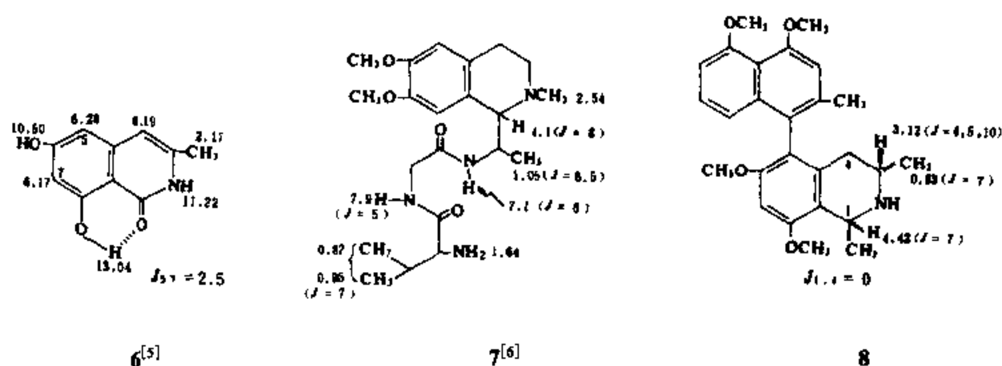
第一节　异喹啉生物碱的^{1}H-NMR 化学位移及偶合常数

一、简单异喹啉生物碱的^{1}H-NMR 化学位移及偶合常数



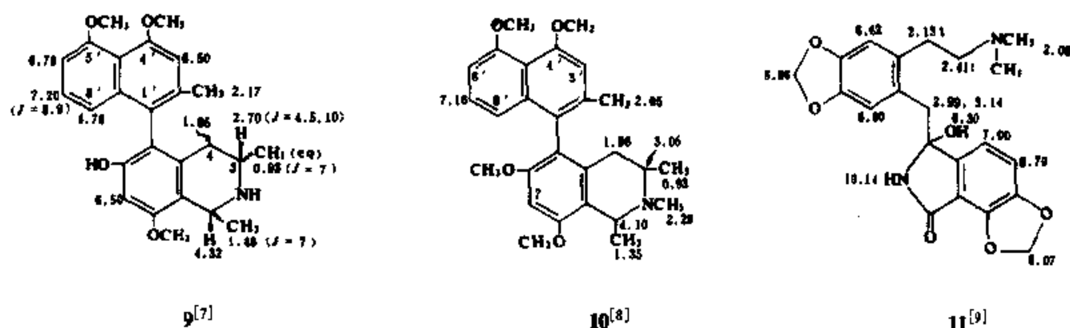
1[1]　2[2]　3[3]　4[4]　5[4]

CH_3O: 3.83, 3.86 CH_3O: 3.87, 3.87, 3.97



6[5]　7[6]　8

OCH_3: 3.82, 3.85; 芳-H 6.56, 6.61



9[7]　10[8]　11[9]

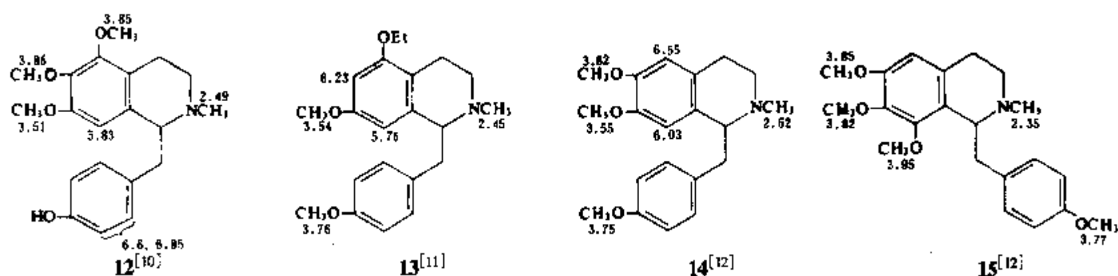
$J_{1,4ax} = 1$　$J_{1-H,1-CH_3} = 7$

4′-, 5′-8-OCH_3 3.95, 3.98, 3.89;

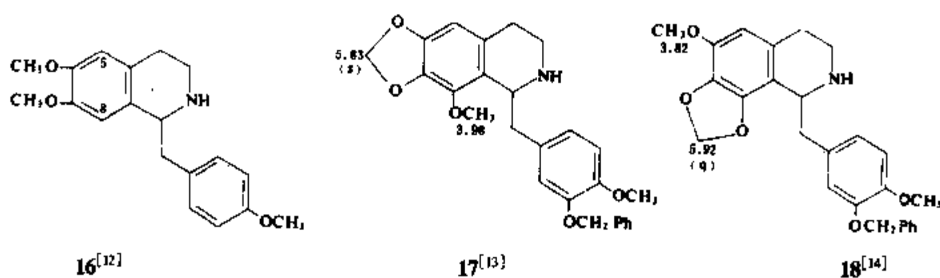
3′-H, 7-H, 6.47, 6.78;

6′-H, 8′-H, 6.85, 6.74

二、苄基异喹啉生物碱的^{1}H-NMR 化学位移及偶合常数



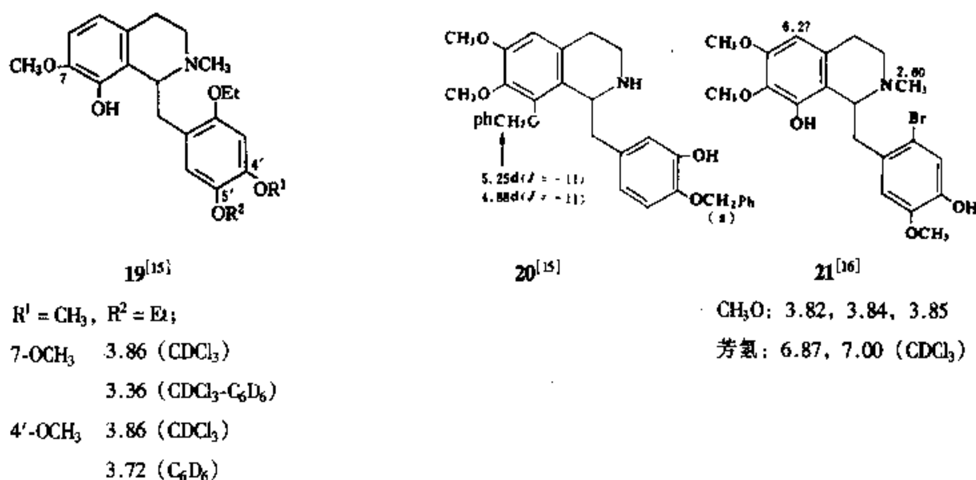
12[10]　13[11]　14[12]　15[12]



16[12]　17[13]　18[14]

CH_3O 3.83, 3.80, 3.78

5-H, 8-H, 6.63, 6.58



19[15]　20[15]　21[16]

$R^1 = CH_3$, $R^2 = Et$;

7-OCH_3　3.86 ($CDCl_3$)

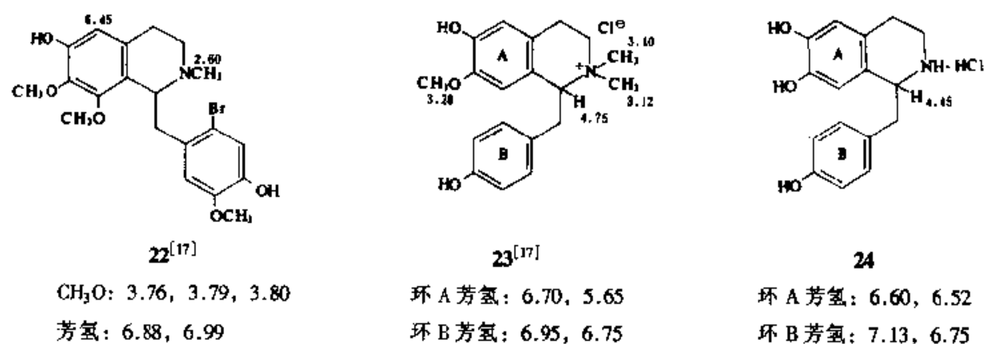
3.36 ($CDCl_3$-C_6D_6)

4'-OCH_3　3.86 ($CDCl_3$)

3.72 (C_6D_6)

21: CH_3O: 3.82, 3.84, 3.85

芳氢: 6.87, 7.00 ($CDCl_3$)



22[17]　23[17]　24

22: CH_3O: 3.76, 3.79, 3.80

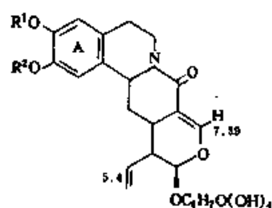
芳氢: 6.88, 6.99

23: 环 A 芳氢: 6.70, 5.65

环 B 芳氢: 6.95, 6.75

24: 环 A 芳氢: 6.60, 6.52

环 B 芳氢: 7.13, 6.75

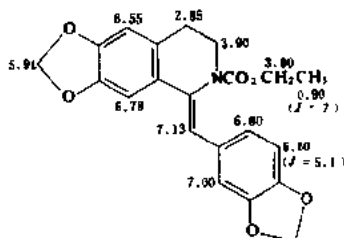


25[18]

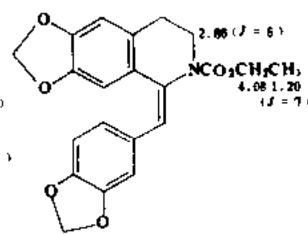
R^1 或 $R^2 = CH_3$ 或 H

CH_3O 3.79

环 A 芳氢 6.75×2



26[19]

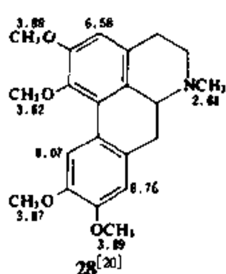


27[19]

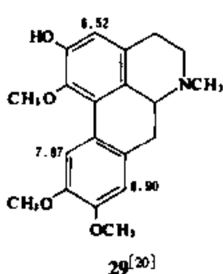
亚甲二氧基：5.92，6.02

芳氢：6.70，6.75，7.21

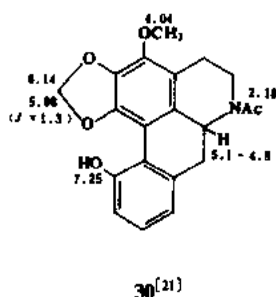
三、阿朴啡生物碱的¹H-NMR 化学位移及偶合常数



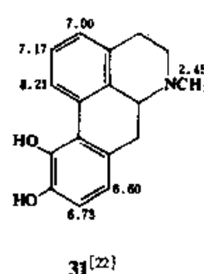
28[20]



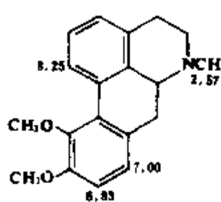
29[20]



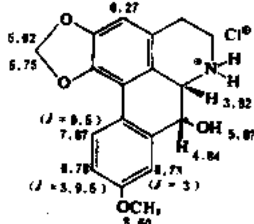
30[21]



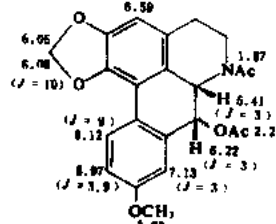
31[22]



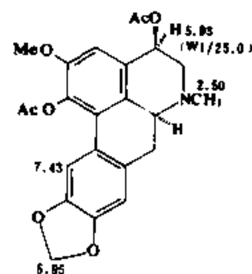
32[23]



33[24]



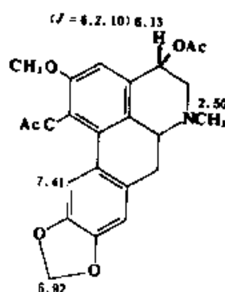
34[24]



35[25]

OAc：2.15，2.30

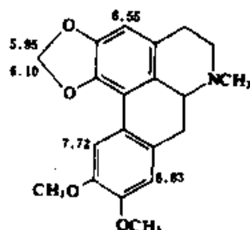
芳氢：6.78，6.88



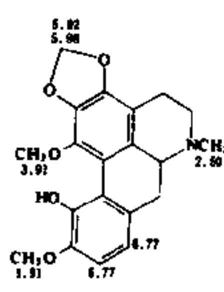
36[25]

OAc：2.13，2.29

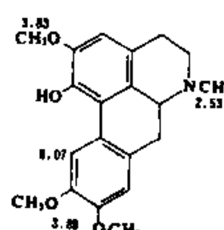
芳氢：6.73，6.77



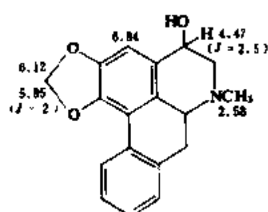
37[26]



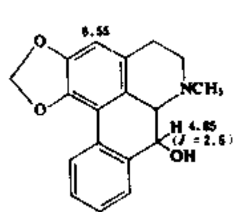
38[27]



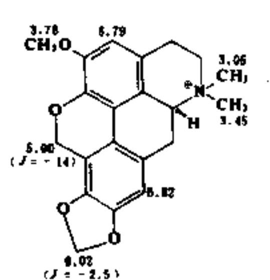
39[28]



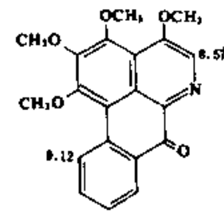
40[29]



41



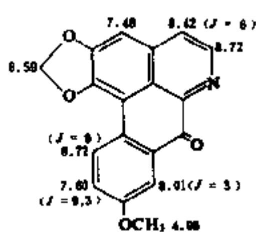
42[30]



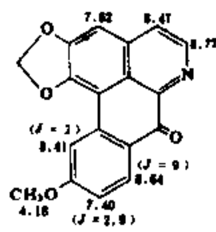
43[31]

OCH_3：4.02，4.07，4.12，4.22

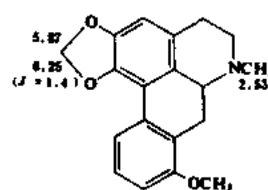
芳氢：8.56，7.80～7.35（3H）



44[32]

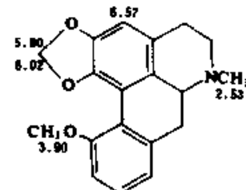


45[33]

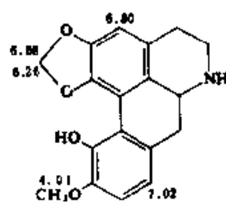


46[34]

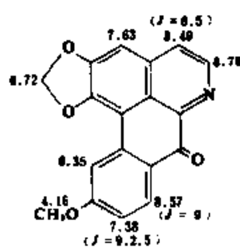
芳氢：6.52～7.80



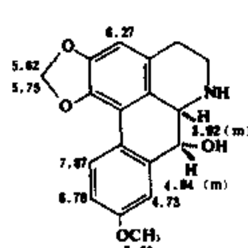
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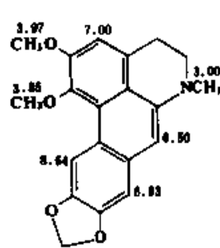
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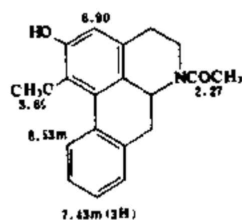
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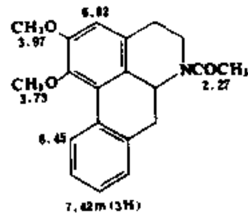
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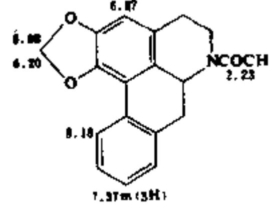
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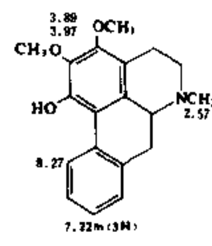
52[34]



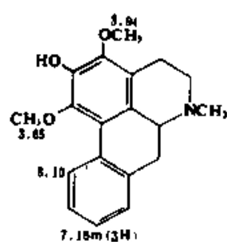
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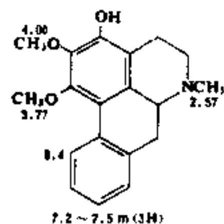
54[34]



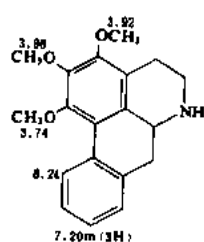
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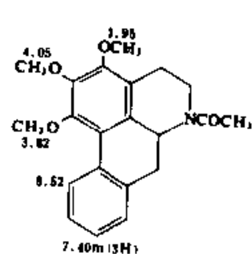
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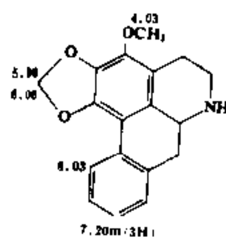
57[34]



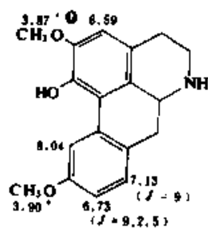
58[34]



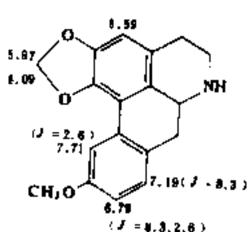
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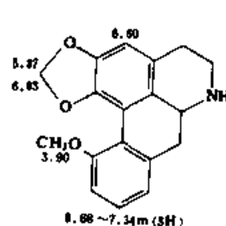
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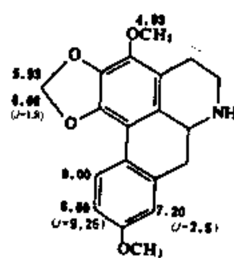
61[34]



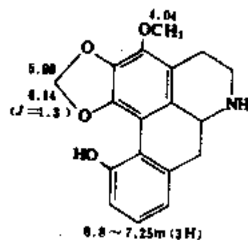
62[34]



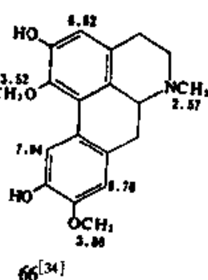
63[34]



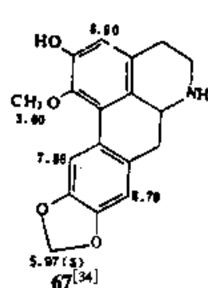
64[34]



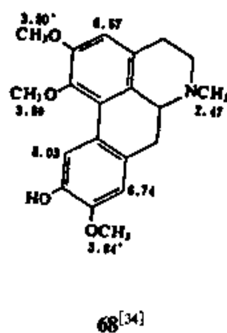
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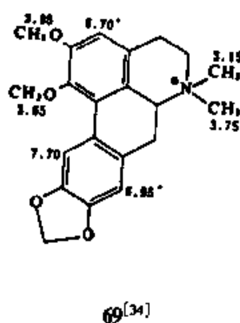
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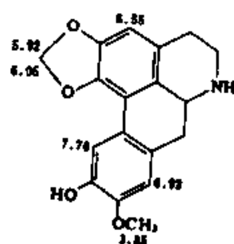
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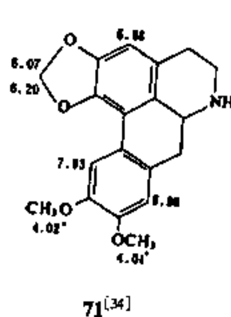
68[34]



69[34]

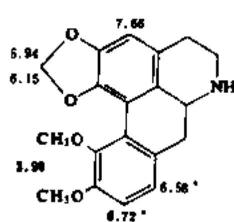


70[34]

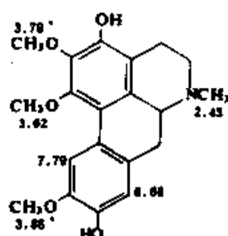


71[34]

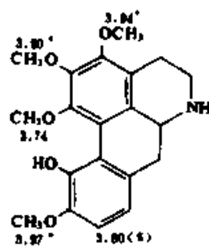
❶ "*"表示两个化学位移可相互交换。以后均同此。



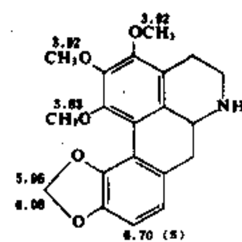
72[34]



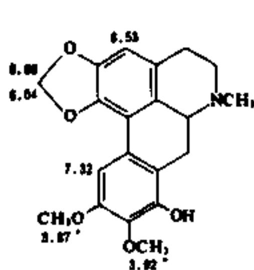
73[34]



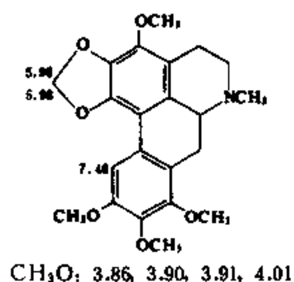
74[34]



75[34]

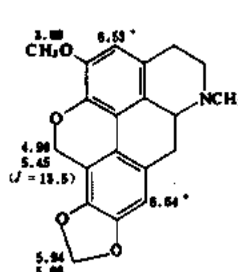


76[34]

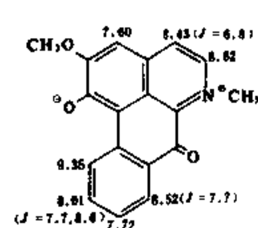


CH_3O: 3.86, 3.90, 3.91, 4.01

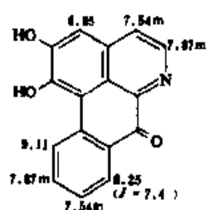
77[34]



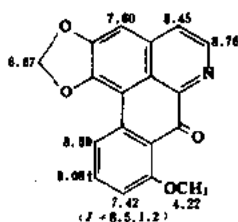
78[34]



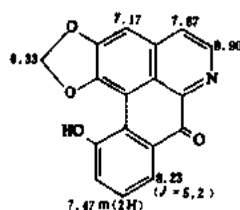
79[34]



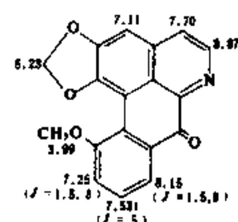
80[34]



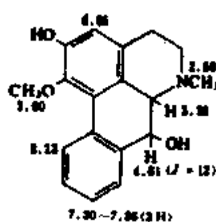
81[34]



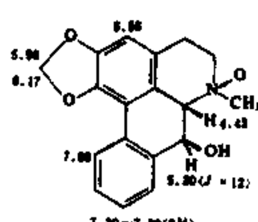
82[34]



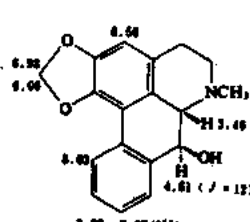
83[34]



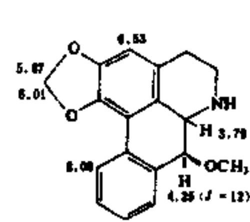
84[34]



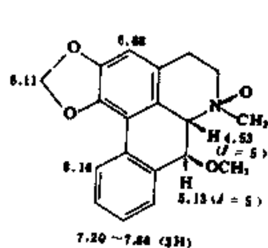
85[34]



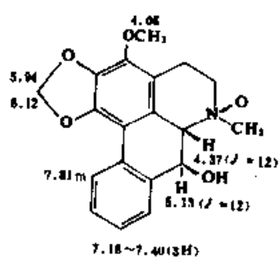
86[34]



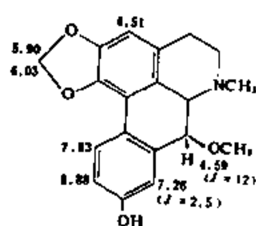
87[34]



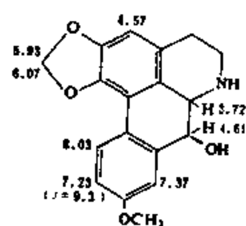
88[34]



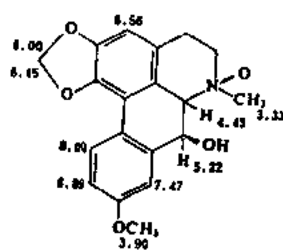
89[34]



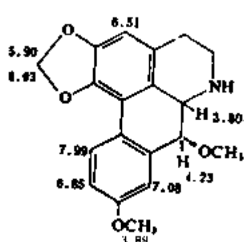
90[34]



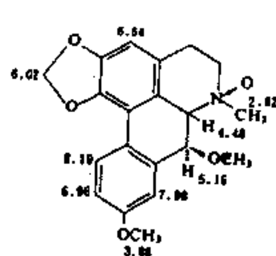
91[34]



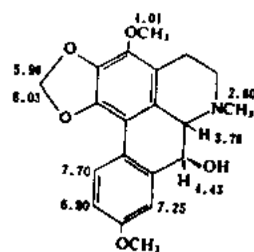
92[34]



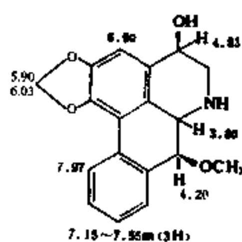
93[34]



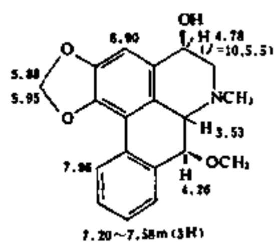
94[34]



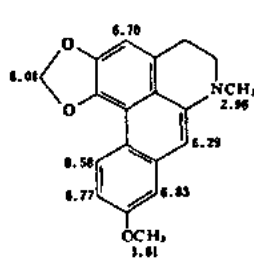
95[34]



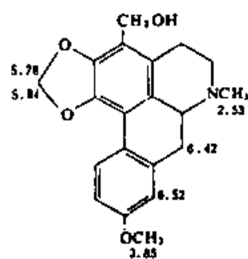
96[34]



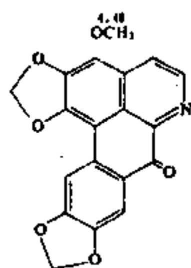
97[34]



98[34]



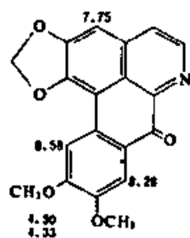
99[34]



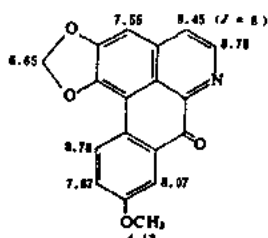
100[35]

亚甲二氧基：6.21，6.60

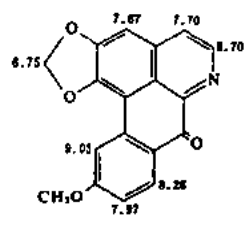
芳氢：7.83，8.18，8.83 (2H)



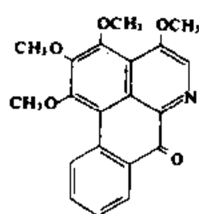
101[36]



102[37]

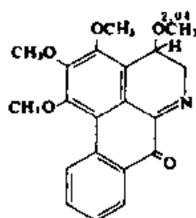


103[38]



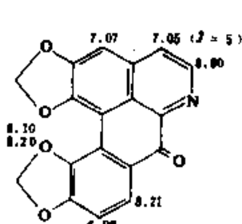
104

CH_3O:4.05, 4.10, 4.15, 4.25

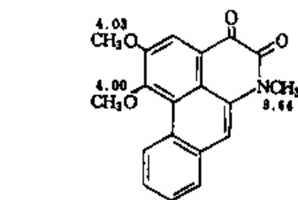


105[39]

CH_3O:4.09, 4.13, 4.22

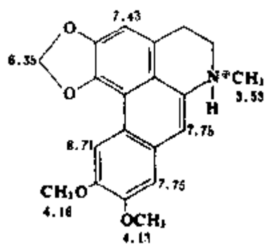


106[40]

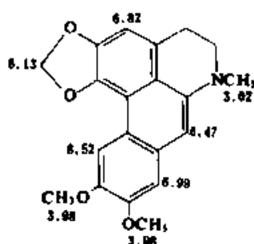


107[41]

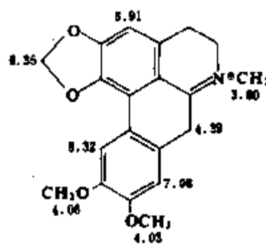
芳氢：7.22，7.5～7.8（3H），7.98，9.37



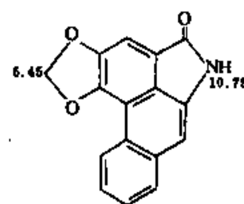
108[42]



109[42]

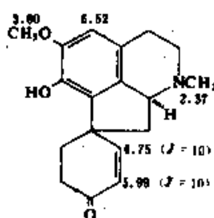


110

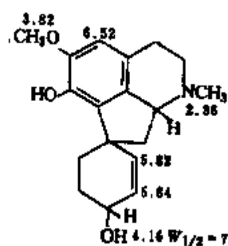


111[43]

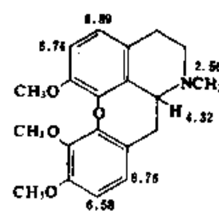
芳氢：7.10，7.60，7.5～7.7（2H）7.9，8.5



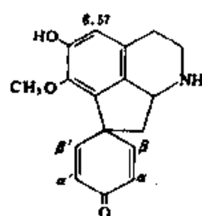
112



113



114



115[44]

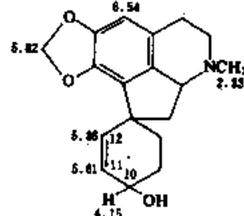
$\delta_\beta = \delta_{\beta'} = 7.04$

$\delta_\alpha = \delta_{\alpha'} = 6.20$

$J_{\beta\beta'} = 2.5$

$J_{\alpha'\beta'} = 10$

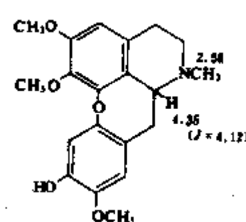
$J_{\alpha\alpha'} = 1.5$



116[45]

$J_{10,11} = 3.1$

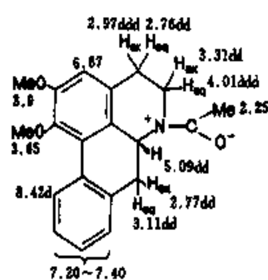
$J_{12,10} = 1.2$



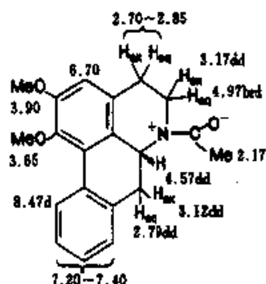
117[46]

CH_3O：3.76，3.80，3.87

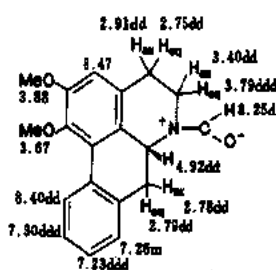
芳氢：6.49（2H），6.87



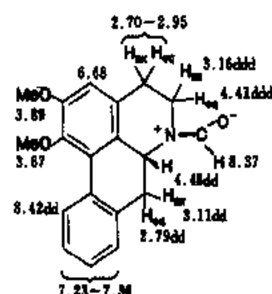
118[346]



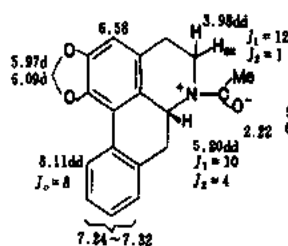
119[346]



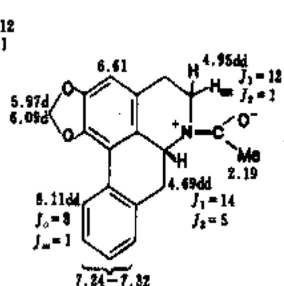
120[346]



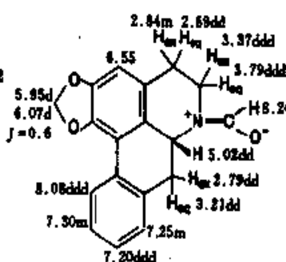
121[346]



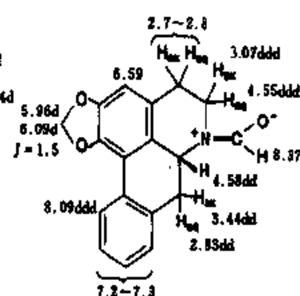
122[346]



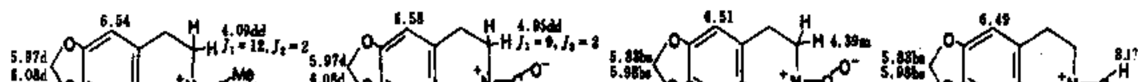
123[346]

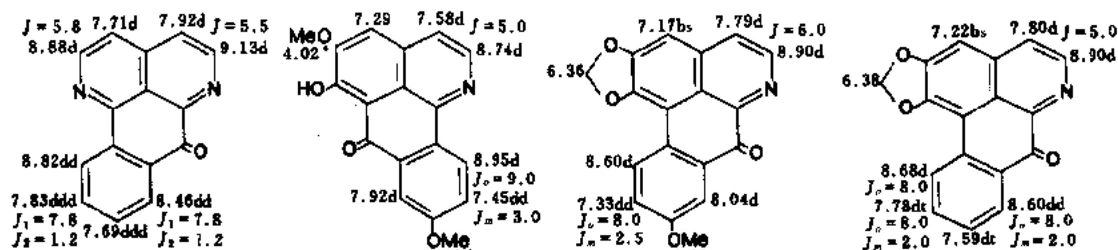


124[346]

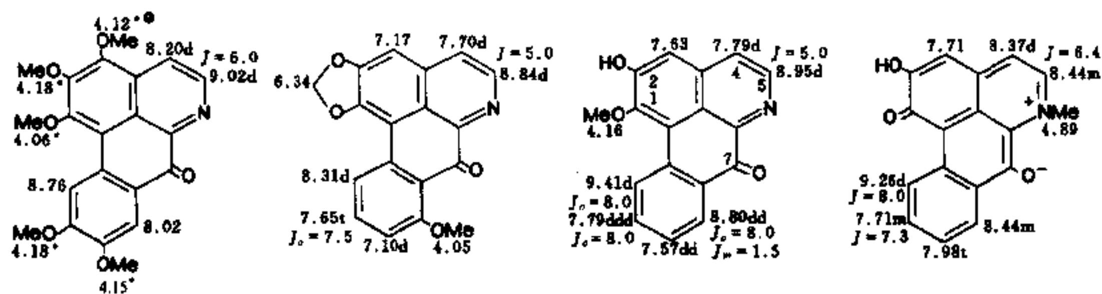


125[346]

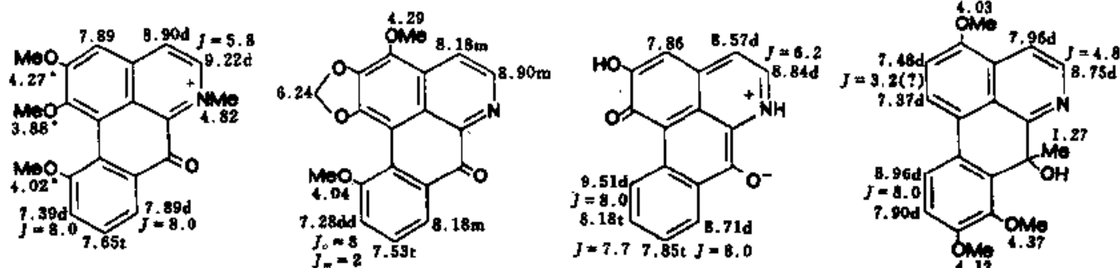




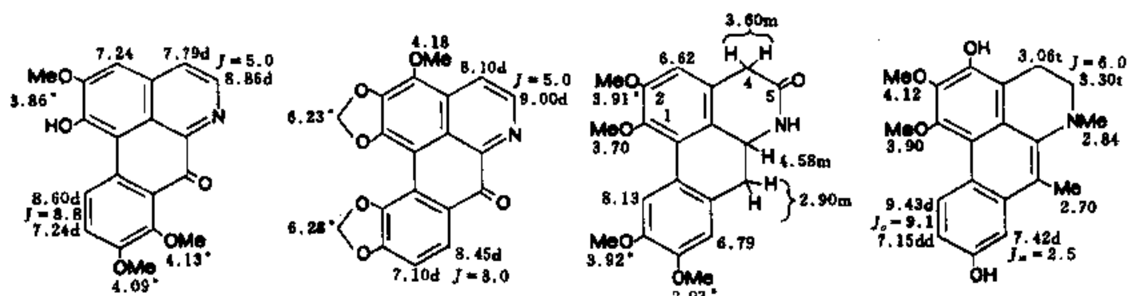
134[348] 135[349] 136[350] 137[350]



138[351] 139[350] 140[352] 141[353]

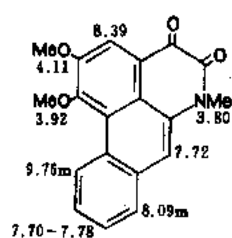


142[354] 143[355] 144[353] 145[356]

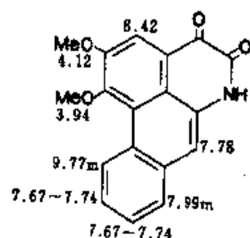


146[357] 147[358] 148[359] 149[360]

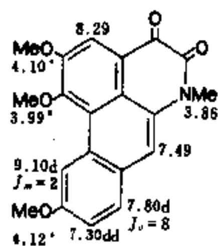
● "*"表示可互换的化学位移值。



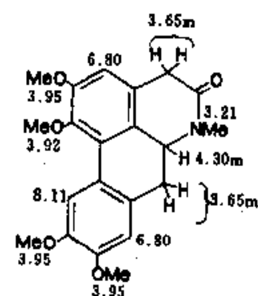
150[361]



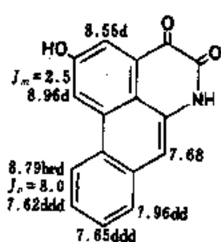
151[361]



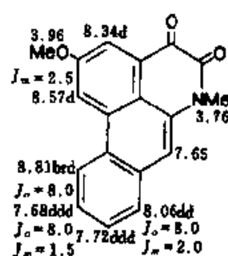
152[362]



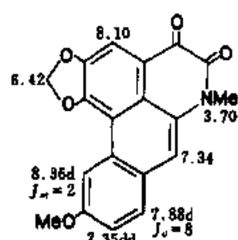
153[360]



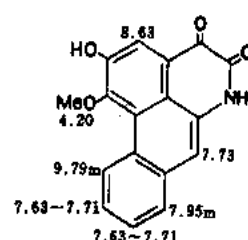
154[352]



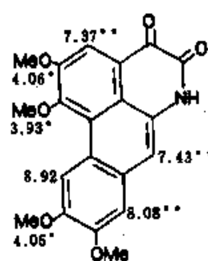
155[352]



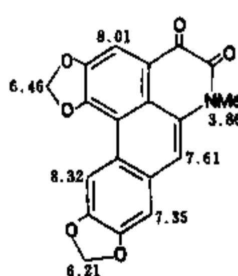
156[362]



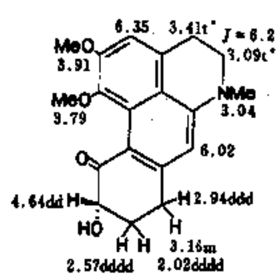
157[352]



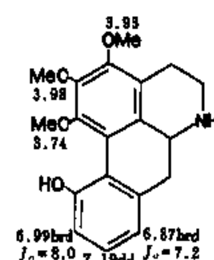
158[363]



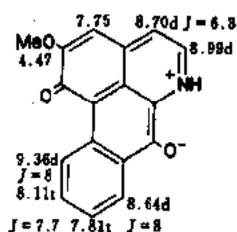
159[364]



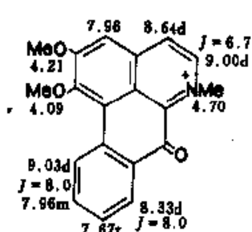
160[365]



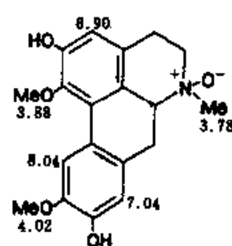
161[366]



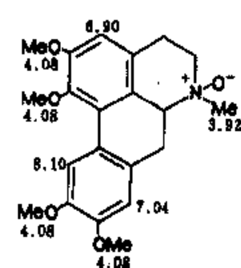
162[353]



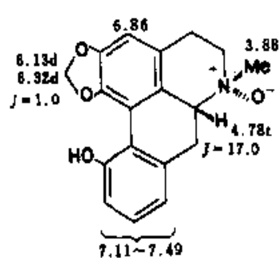
163[353]



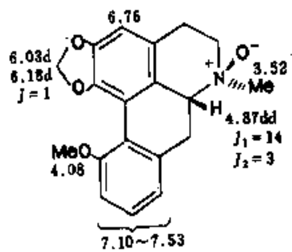
164[367]



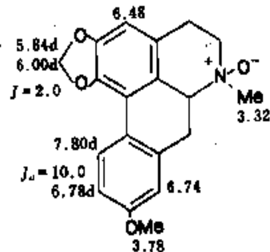
165[367]



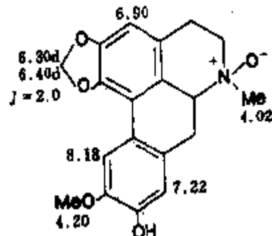
166[368]



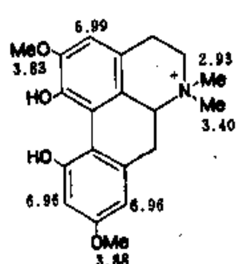
167[368]



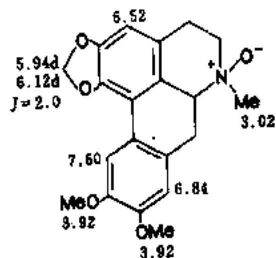
168[367]



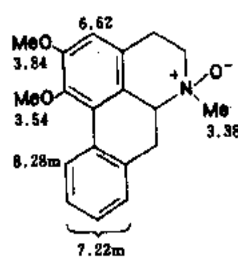
169[367]



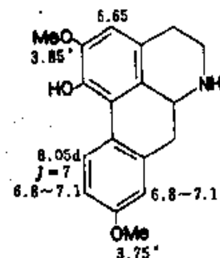
170[369]



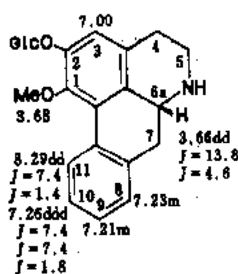
171[367]



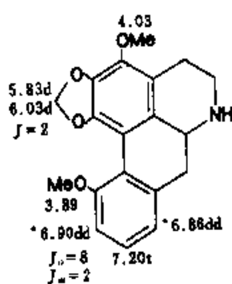
172[367]



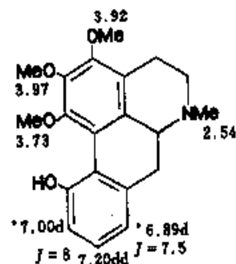
173[370]



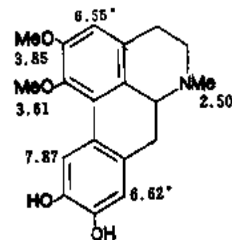
174[371]



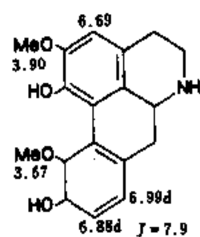
175[372]



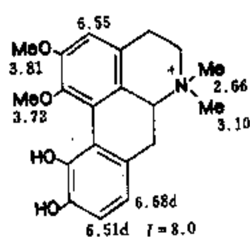
176[366]



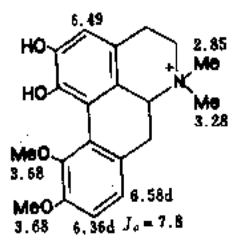
177[373]



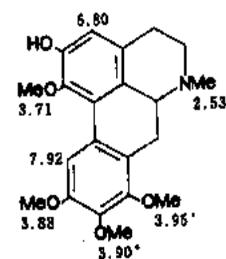
178[374]



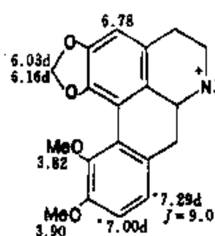
179[373]



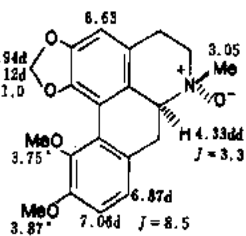
180[375]



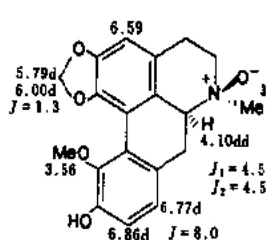
181[369]



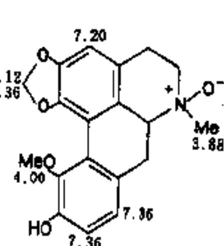
182[376]



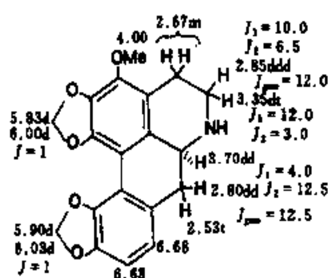
183[377]



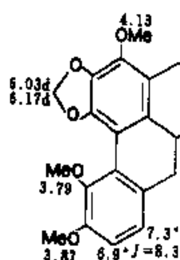
184[367]



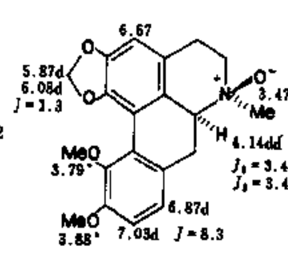
185[377]



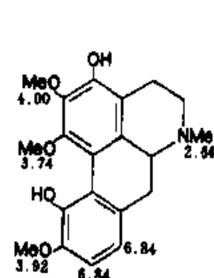
186[378]



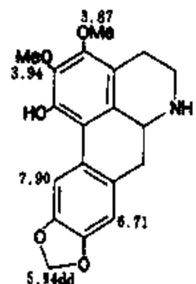
187[376]



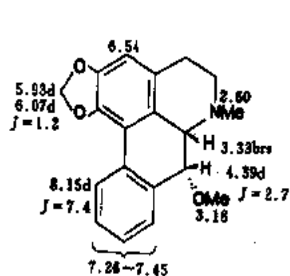
188[377]



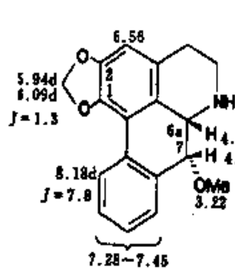
189[379]



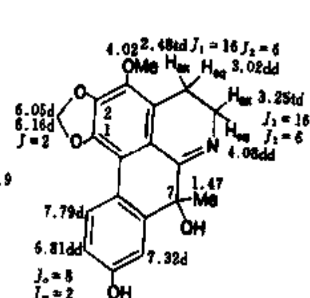
190[380]



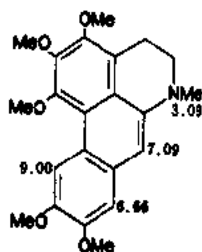
191[381]



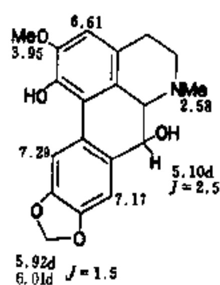
192[381]



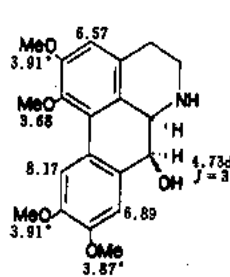
193[372]



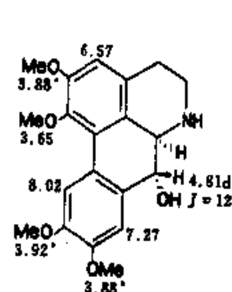
194[382]



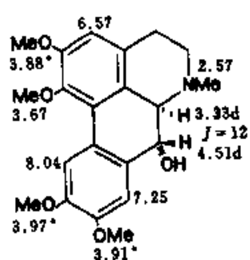
195[383]



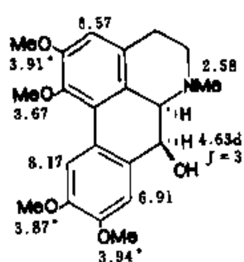
196[384]



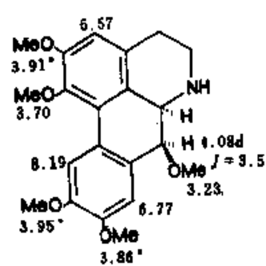
197[384]



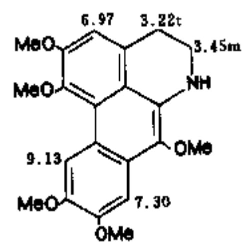
198[384]



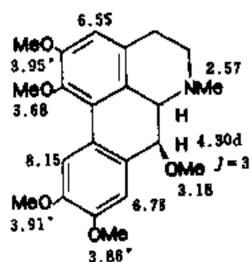
199[384]



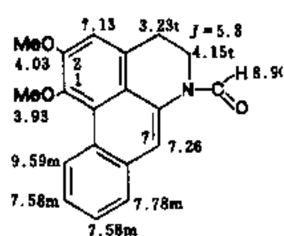
200[384]



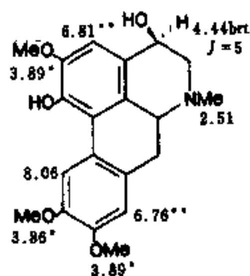
201[384]



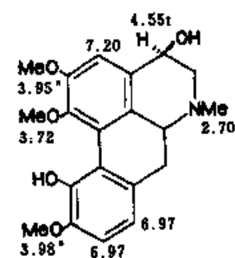
202[384]



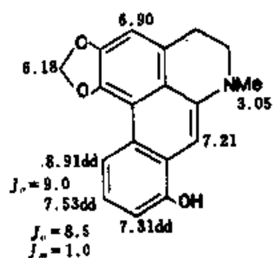
203[385]



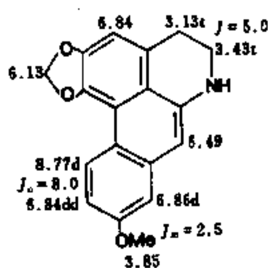
204[386]



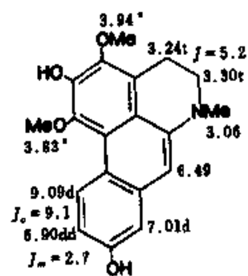
205[387]



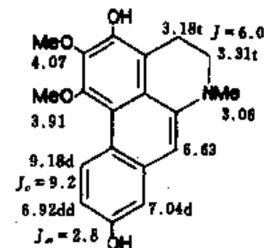
206[388]



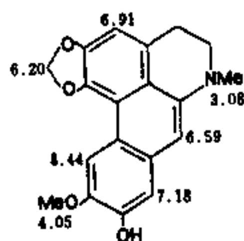
207[389]



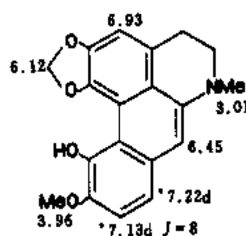
208[390]



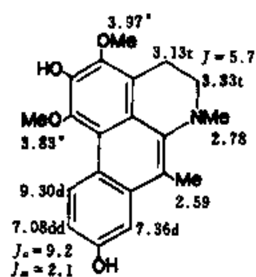
209[390]



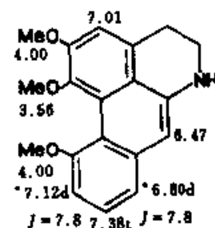
210[391]



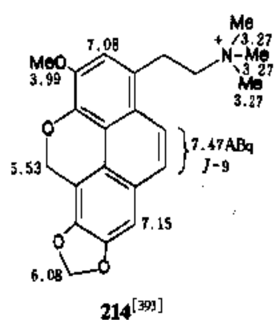
211[392]



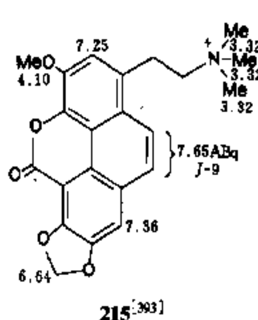
212[390]



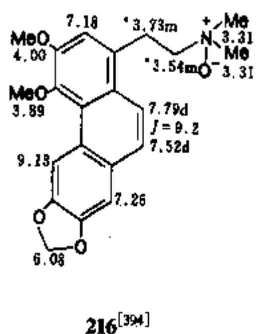
213[354]



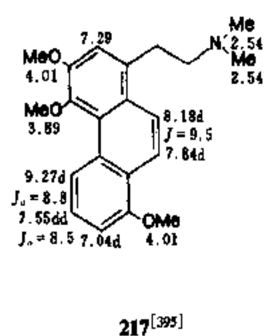
214[393]



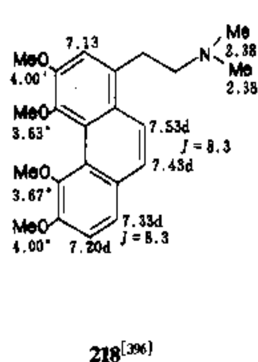
215[393]



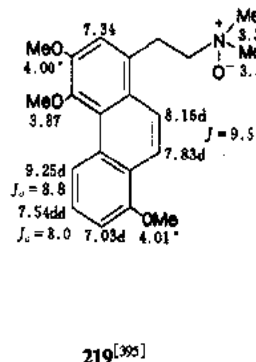
216[394]



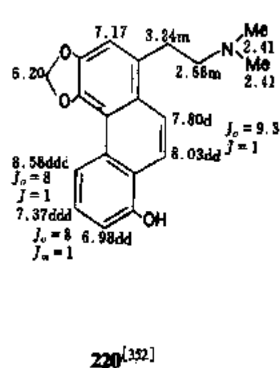
217[395]



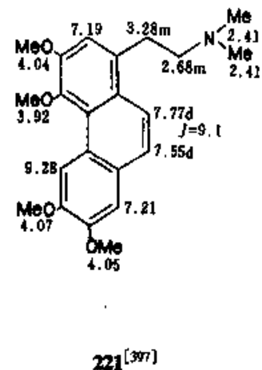
218[396]



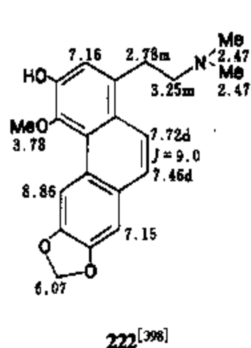
219[395]



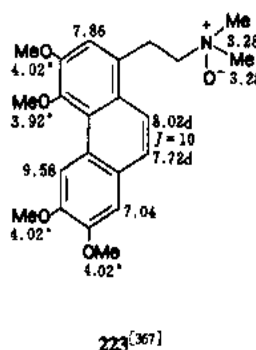
220[352]



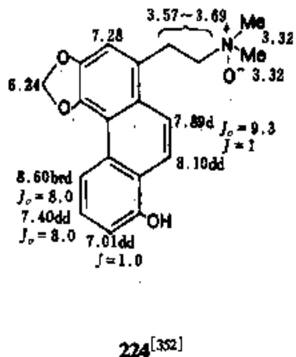
221[397]



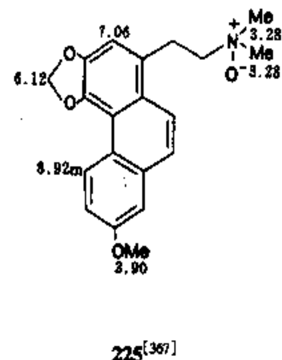
222[398]



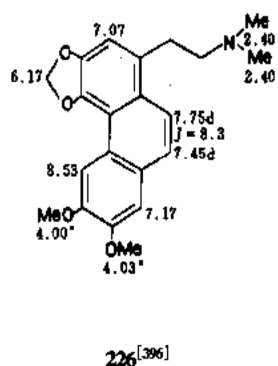
223[367]



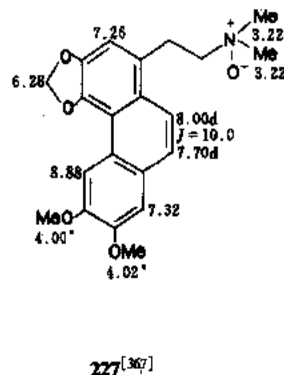
224[352]



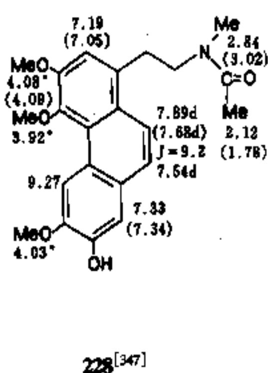
225[367]



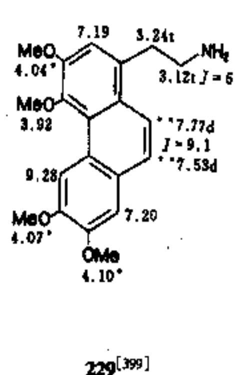
226[396]



227[367]

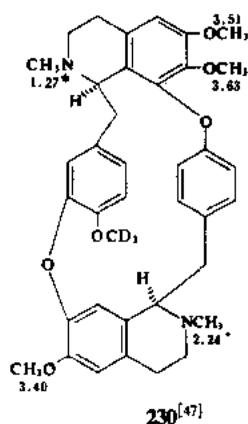


228[347]

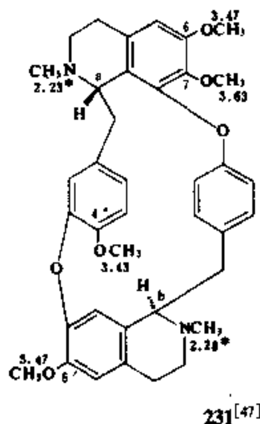


229[399]

四、双苄基异喹啉生物碱的¹H-NMR化学位移及偶合常数



230[47]



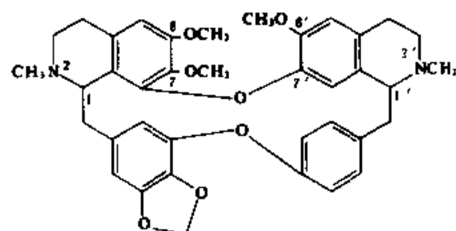
231[47]

a，b = *R*，*R* 或 *S*，*S*

$\delta_{7\text{-}OCH_3} = 3.62$，

$\delta_{4''\text{-}OCH_3} = 3.30$；

$\delta_{6\text{-}OCH_3} = \delta_{6'\text{-}OCH_3} = 3.52$，3.42



232[48]（1*R*，1′*S*）：

$\delta_{6\text{-}OCH_3} = 3.75$；$\delta_{6'\text{-}OCH_3} = 3.60$

$\delta_{7\text{-}OCH_3} = 3.16$；$\delta_{2'\text{-}NCH_3} = 2.58$

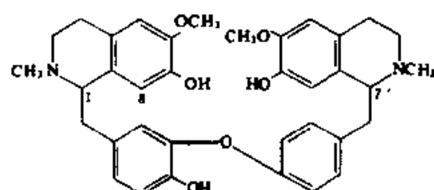
$\delta_{2\text{-}N\text{-}CH_3} = 2.30$

233[48]（1*S*，1′*S*）：

$\delta_{6\text{-}OCH_3} = 3.78$；$\delta_{6'\text{-}OCH_3} = 3.33$

$\delta_{7\text{-}OCH_3} = 3.18$；$\delta_{2'\text{-}NCH_3} = 2.63$

$\delta_{2N\text{-}CH_3} = 2.32$

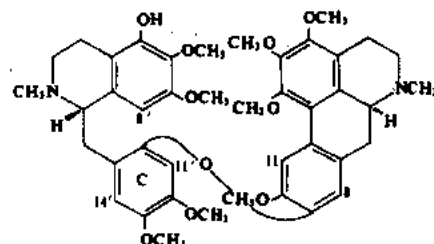


234[49]（1*S*，1′*S*）：

$\delta_{OCH_3} = 3.81$

$\delta_{NCH_3} = 2.43$，2.48

$\delta_{8\text{-}H} = 6.24$，6.29



235[49]（1*R*，1′*S*）：

$\delta_{OCH_3} = 3.82$，3.84

$\delta_{NCH_3} = 2.44$，2.49

$\delta_{8\text{-}H} = 6.22$，6.33

236[50]

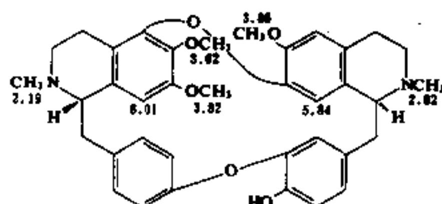
$\delta_{OCH_3} = 3.47$，3.70，

3.73，3.76，3.83，3.89

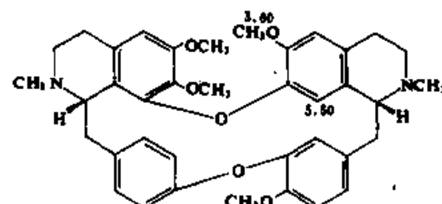
$\delta_{8'\text{-}H} = 5.71$；$\delta_{11'\text{-}H} = 6.43$；

$\delta_{14\text{-}H} = 6.48$；$\delta_{8\text{-}H} = 6.66$；

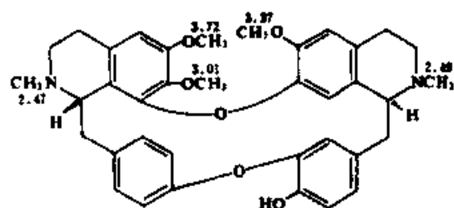
$\delta_{11\text{-}H} = 7.98$



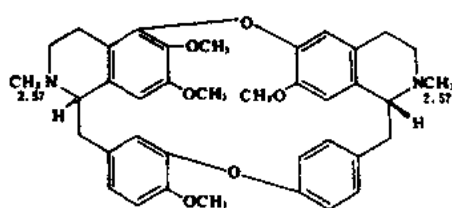
237[51]



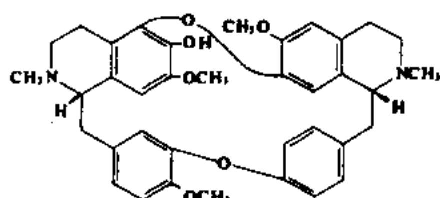
238[52]



239[51]



240[53]



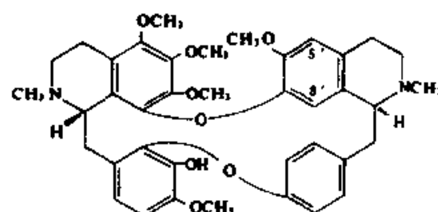
241[54]

NCH_3：2.55，2.40

OCH_3：3.92，3.82，3.46

芳氢：5.02，5.24，5.82

6.61，6.42～7.26（4H）



242[55]

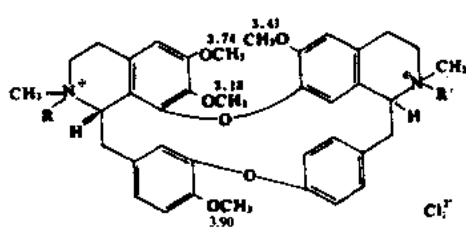
NCH_3：2.58，2.45

OCH_3：3.89，3.82，3.77，

3.36，3.16

5′-H：6.39

8′-H：5.90



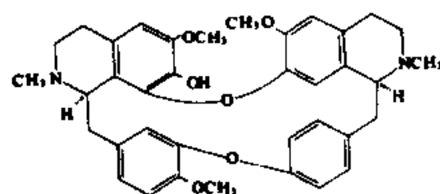
243[55]

NCH_3：2.50，2.78

芳氢：5.9～7.3（10H）

R＝H，R′＝CH_3

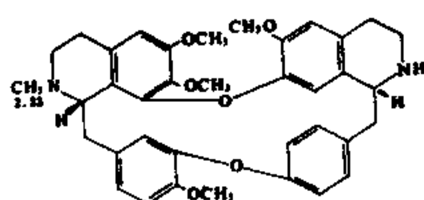
R＝CH_3，R′＝H



244[56]

NCH_3：2.43，2.25

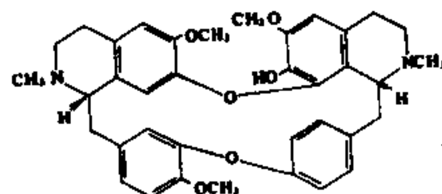
OCH_3：3.88，3.88，3.73



245[56]

OCH_3：3.88，3.70，3.38，3.22

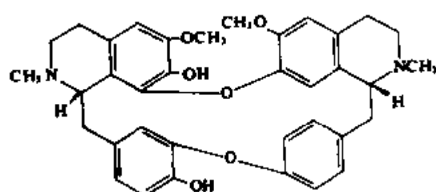
芳氢：6.9～7.4（10H）



246

NCH_3：2.53，2.47

OCH_3：3.93，3.73，3.29



247[57]

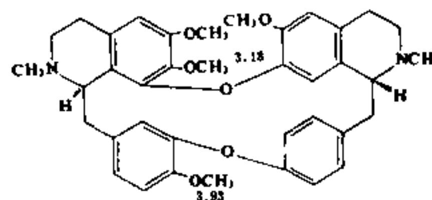
NCH_3: 2.28, 2.58

OCH_3: 3.30, 3.73

芳氢: 5.97 (1H), 7.11 (J=8, 2H),

7.32 (J=8, 2H),

6.28~6.75 (5H)

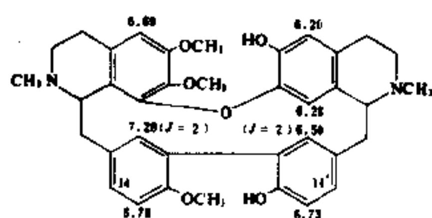


248[57]

NCH_3: 2.33, 2.62

OCH_3: 3.18, 3.37, 3.74, 3.94

芳氢: 6.00 (1H), 6.30~7.26 (9H)

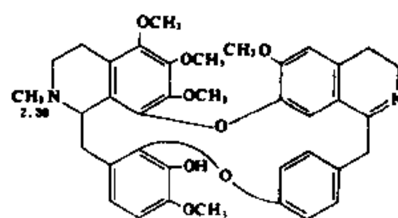


249[58]

NCH_3: 2.57, 2.29

OCH_3: 3.80, 3.70, 3.38

14-H, 14'-H: 7.25~7.08

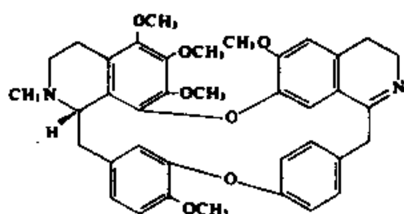


250[59]

OCH_3: 3.88, 3.83, 3.79,

3.55, 3.21

芳氢: 6.42~7.58



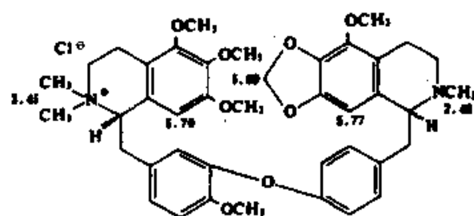
251[59]

NCH_3: 2.33, 2.28

OCH_3: 3.93, 3.91, 3.88, 3.83, 3.78,

3.63, 3.52, 3.46, 3.39, 3.83

(2种构象元)

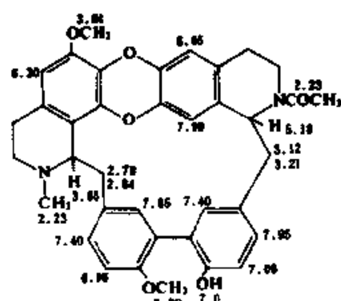


252[60]

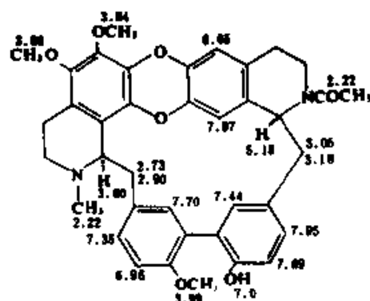
OCH_3: 3.85, 3.80, 3.80,

3.77, 3.63

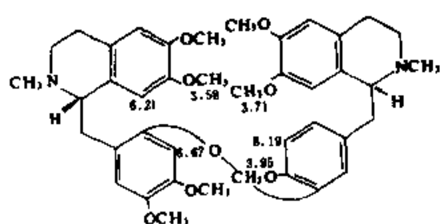
芳氢: 6.98, 6.63 (J=8, 4H)



253[61]



254[61]

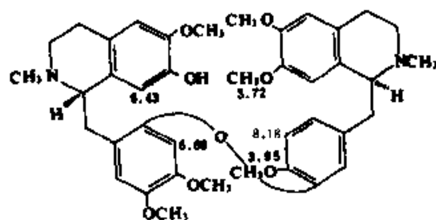


255[62]

NCH_3：2.45，2.48

OCH_3：3.80，3.80，3.83，3.91

芳氢：6.53，6.56，6.60，6.62

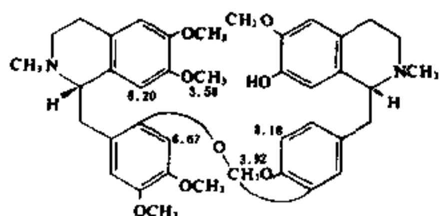


256[63]

NCH_3：2.42，2.48

OCH_3：3.88，3.79，3.79，3.79

芳氢：6.60，6.60，6.55，6.52

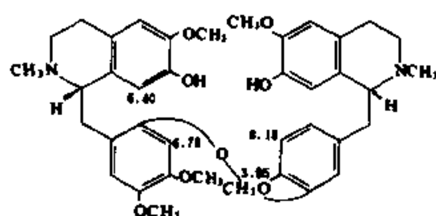


257[64]

NCH_3：2.50，2.47

OCH_3：3.78，3.78，3.82，3.88

芳氢：6.55，6.55，6.55，6.59

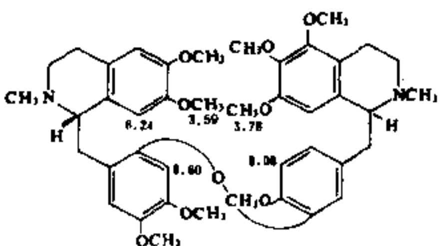


258[65]

NCH_3：2.49，2.52

OCH_3：3.79，3.83，3.83，3.92

芳氢：6.51，6.57，6.57，6.57

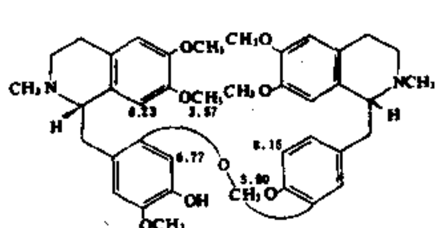


259[62]

NCH_3：2.44，2.47

OCH_3：3.78，3.78，3.82，3.89，3.94，3.96

芳氢：6.55，6.55，6.60

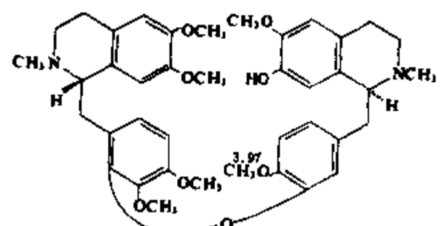


260[62]

NCH_3：2.47，2.48

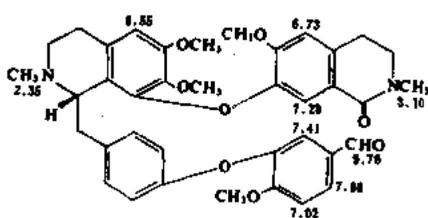
OCH_3：3.75，3.78，3.88

芳氢：6.50，6.50，6.50，6.57



261

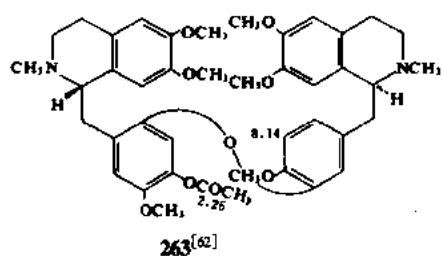
芳氢：6.14，6.42，6.52，6.52，
6.75，6.81，8.12



262[66]

OCH_3：3.94，3.90，3.85，3.62

芳氢：6.80，7.18（$J=8.5$）



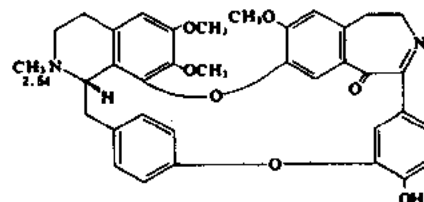
263[62]

NCH_3: 2.57, 2.61

OCH_3: 3.54, 3.67, 3.70,

3.84, 3.85, 3.90

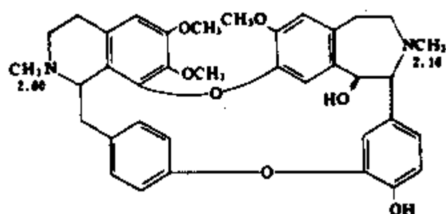
芳氢：6.40, 6.54, 6.54, 6.60, 6.87



264

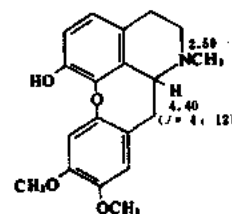
OCH_3：3.96, 3.85, 3.37

芳氢：3.78～5.60



265[67]

OCH_3：3.68, 3.40, 3.18

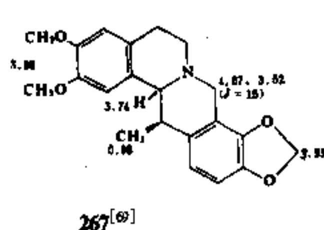


266[68]

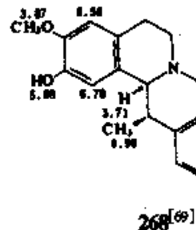
OCH_3：3.80, 3.82

芳氢：6.58, 6.58, 6.76, 6.82

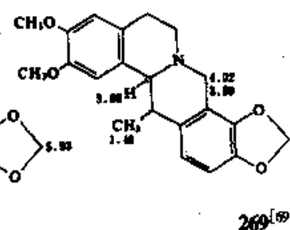
五、原小蘖碱和普托品类生物碱的^{1}H-NMR化学位移及偶合常数



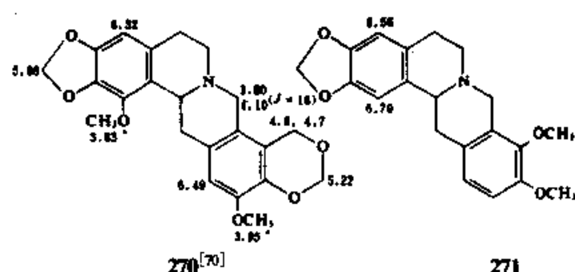
267[69]



268[69]

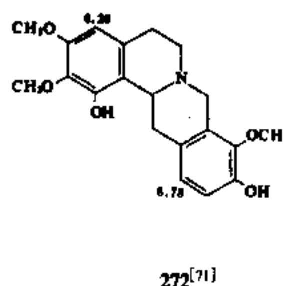


269[69]



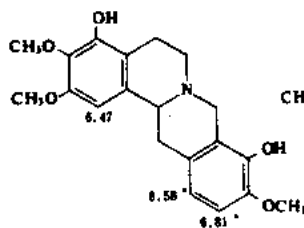
270[70]

271



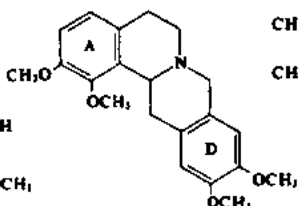
272[71]

OCH_3：3.81, 3.85, 3.93



273[72]

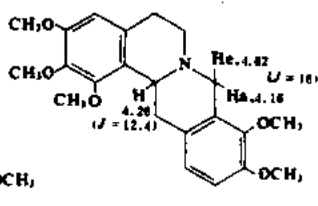
OCH_3：3.69，3.79，3.79



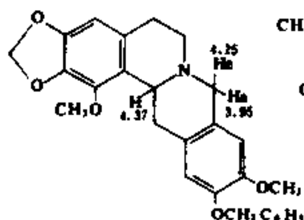
274

芳氢：6.18（D环），

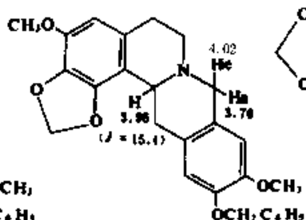
6.87（A环）



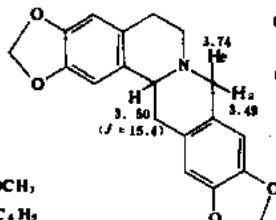
275[73]



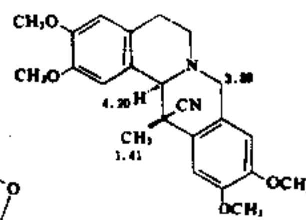
276[73]



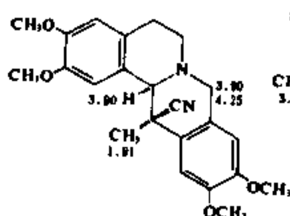
277



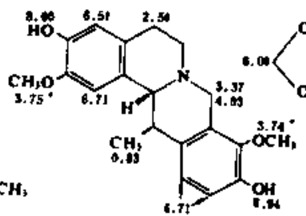
278[74]



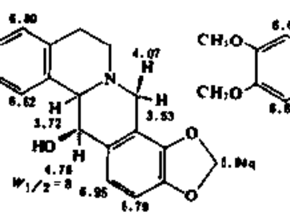
279[75]



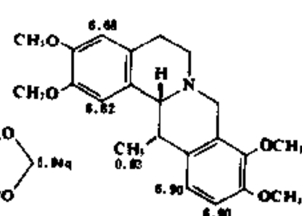
280



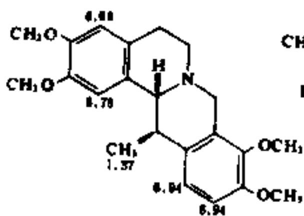
281[76]



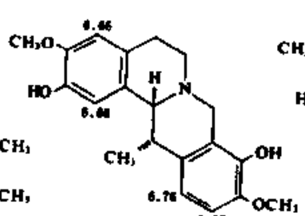
282[77]



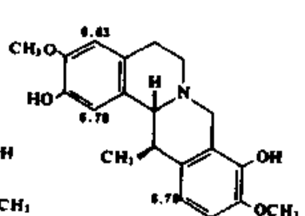
283



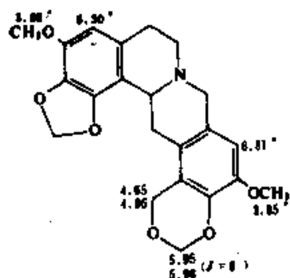
284[78]



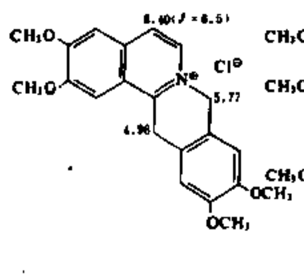
285[78]



286



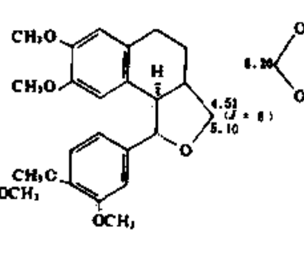
287[79]



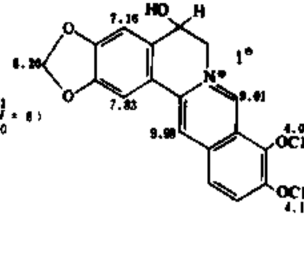
288[80]

OCH_3：3.83，3.83，4.07，4.13

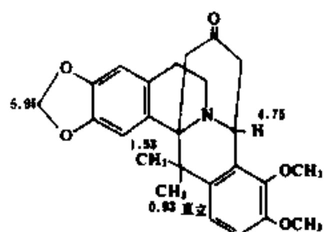
芳氢：7.16，7.28，7.74，7.97



289[81]

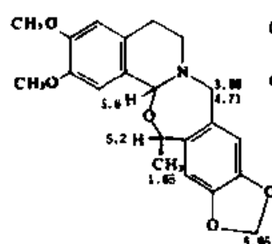


290[82]



291[83]

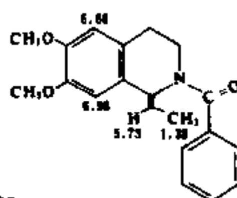
OCH_3: 3.83, 3.92



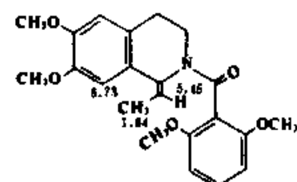
292[84]

OCH_3: 3.82, 3.88

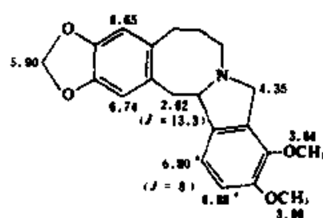
芳氢: 6.55, 6.75, 6.75, 6.82



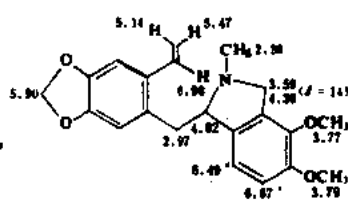
293[85]



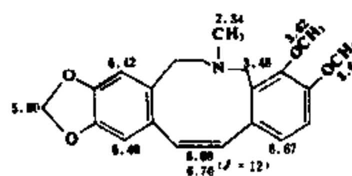
294



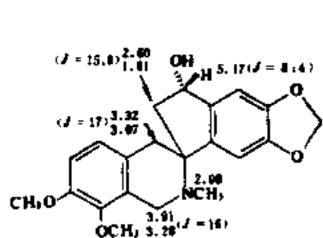
295[86]



296[86]

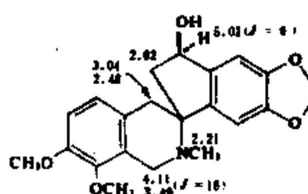


297[87]



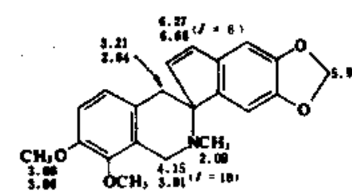
298[88]

芳氢: 6.71, 6.81, 6.76



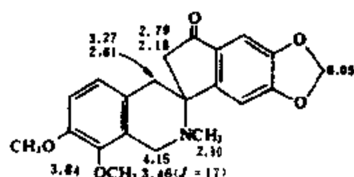
299[88]

芳氢: 6.73, 6.79



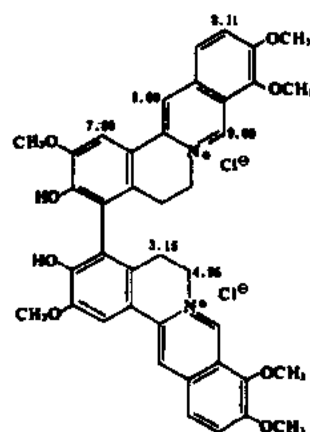
300[88]

芳氢: 6.76



301[88]

芳氢: 7.05, 6.98, 6.73



302[89]

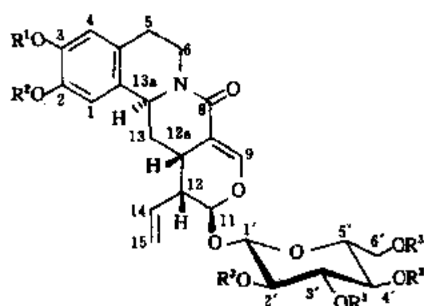
表 6-1 生物碱 303 ~ 312 的 ^{1}H-NMR 化学位移[400]

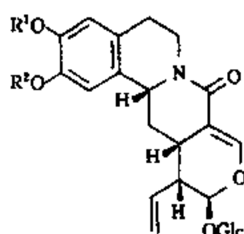
质子 \ 化合物	307	308	303	304	305
1-H	6.690s	6.78s	6.83s	6.72s	6.80s
3-H	—	—	—	—	—
4-H	6.693 s	6.57s	6.74s	6.71s	6.59s
5-H	2.66dt (15.5,3.0)	2.60dt (15.5,3.0)	2.70m	2.68ddd (16.0,4.5,2.0)	2.62ddd (16.0,4.5,2.0)
	2.76ddd (15.5,11.5,4.0)	2.71ddd (15.5,12.5,4.5)	2.99ddd (15.5,11.5,5.5)	2.96ddd (16.0,11.0,6.0)	2.92ddd (16.0,12.0,6.0)
6-H	2.88td (11.5,3.0)	2.84td (12.5,3.0)	3.05m	3.06ddd (12.5,11.0,4.5)	3.04td (12.0,4.5)
	4.71ddd (11.5,4.0,3.0)	4.73ddd (12.5,4.5,3.0)	4.68ddd (12.0,5.5,2.0)	4.64ddd (12.5,6.0,2.0)	4.65ddd (12.0,6.0,2.0)
9-H	7.41d(2.5)	7.41d(2.5)	7.33d(2.5)	7.32d(2.5)	7.33d(2.5)
11-H	5.49d(1.5)	5.49d(1.5)	5.42d(1.5)	5.41d(1.5)	5.42d(1.5)
12-H	2.70ddd (10.0,5.5,1.5)	2.71ddd (10.0,5.5,1.5)	2.70m	2.67ddd (10.5,5.5,1.5)	2.70ddd (10.0,5.5,1.5)
12a-H	3.19dddd (13.0,5.5,3.5, 2.5)	3.21dddd (13.0,5.5,3.5, 2.5)	2.85dddd (12.5,5.5,4.5, 2.5)	2.87dddd (13.0,5.5,4.5, 2.5)	2.87dddd (12.5,5.5,4.5, 2.5)
13-H	1.35td(13.0,11.0)	1.36td(13.0,11.5)	2.00ddd (14.0,12.5,5.5)	1.96ddd (14.0,13.0,5.5)	1.99ddd (14.0,12.5,5.0)
	2.30dt(13.0,3.5)	2.37dt(13.0,3.5)	2.46ddd (14.0,4.5,3.0)	2.35ddd (14.0,4.5,3.0)	2.45ddd (14.0,4.5,3.0)
13a-H	4.72dd(11.0,3.5)	4.76dd(11.5,3.5)	4.78br t(4.5)	4.72br t(4.5)	4.76br t(4.0)
14-H	5.52dt(17.0,10.0)	5.53dt(17.0,10.0)	5.67dt(17.0,10.0)	5.66dt(17.0,10.5)	5.67dt(17.0,10.0)
15-H	5.19dd(10.0,2.0)	5.19dd(10.0,2.0)	5.32dd(10.0,2.0)	5.31dd(10.5,2.0)	5.32dd(10.0,2.0)
	5.28dd(17.0,2.0)	5.28dd(17.0,2.0)	5.39dd(17.0,2.0)	5.38dd(17.0,2.0)	5.39dd(17.0,2.0)
1'-H	4.69d(8.0)	4.69d(8.0)	4.61d(8.0)	4.61d(8.0)	4.62d(8.0)
2'-H	3.20dd(9.0,8.0)	3.19dd(9.0,8.0)	3.06dd(9.0,8.0)	3.06dd(9.0,8.0)	3.06dd(9.0,8.0)
3'-H	3.38t(9.0)	3.38t(9.0)	3.30t(9.0)	3.30t(9.0)	3.29t(9.0)
4'-H	3.29dd(9.5,9.0)	3.28dd(9.5,9.0)	3.23t(9.0)	3.23t(9.0)	3.23dd(9.5,9.0)
5'-H	3.32ddd (9.5,5.5,2.0)	3.33ddd (9.5,5.5,2.0)	3.28ddd (9.0,6.0,2.0)	3.28ddd (9.0,5.5,2.0)	3.28ddd (9.5,5.5,2.0)
6'-H	3.68dd(12.0,5.5)	3.67dd(12.0,5.5)	3.64dd(12.0,6.0)	3.65dd(12.0,5.5)	3.65dd(12.0,5.5)
	3.90dd(12.0,2.0)	3.89dd(12.0,2.0)	3.87dd(12.0,2.0)	3.87dd(12.0,2.0)	3.87dd(12.0,2.0)
OMe	3.83s	3.82s	3.80s	3.82s	3.85s
	—	—	3.83s	—	—

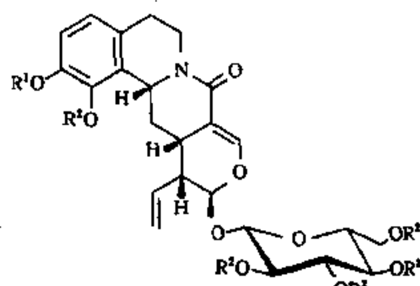
质子 \ 化合物	311	312	309	310	306
1-H	—	—	6.65s	6.82s	6.68s
3-H	6.65d(8.0)	6.81d(8.0)	—	—	—
4-H	6.48d(8.0)	6.61d(8.0)	6.55s	6.73s	6.55s
5-H	2.58 ~ 2.71m	2.61 ~ 2.73m	2.58dt(15.5,3.0)	2.68dt(15.0,2.5)	2.61ddd (16.0,5.0,2.5)
	2.58 ~ 2.71m	2.61 ~ 2.73m	2.70m	2.77ddd (15.0,11.5,3.5)	2.86 ~ 2.94m

续表

质子 \ 化合物	311	312	309	310	306
6-H	2.58~2.71m	2.61~2.73m	2.89td(12.5,3.0)	2.84td(11.5,2.5)	3.05ddd (13.0,11.5,5.0)
			4.64dt(12.5,3.5)		4.61ddd (13.0,6.5,2.5)
9-H	7.45d(2.5)	7.45d(2.5)	7.41d(2.5)	7.42d(2.5)	7.32d(2.5)
11-H	5.50d(1.5)	5.50d(2.0)	5.49d(1.5)	5.50d(2.0)	5.41d(1.5)
12-H	2.58~2.71m	2.61~2.73m	2.70ddd (10.0,5.5,1.5)	2.72ddd (10.0,5.5,2.0)	2.66ddd (10.0,5.5,1.5)
12a-H	3.24m	3.24m	3.19m	3.22dddd (13.0,5.5,3.5, 2.5)	2.86~2.94m
13-H	1.14td(13.0,11.0)	1.14td(13.0,11.0)	1.36td(13.0,11.5)	1.36td(13.0,11.5)	1.95ddd (14.0,12.5,5.5)
	2.77ddd (13.0,3.5,2.0)	2.76ddd (13.0,4.0,2.5)	2.29dt(13.0,3.5)	2.39dt(13.0,3.5)	2.34ddd (14.0,4.5,3.0)
13a-H	4.98dd(11.0,2.0)	4.99dd(11.0,2.5)	4.70dd(11.5,3.5)		4.70br t(4.5)
14-H	5.50dt(17.0,10.5)	5.50dt(17.0,10.0)	5.52dt(17.0,10.0)	5.53dt(18.0,10.0)	5.66dt(17.0,10.0)
15-H	5.15dd(10.5,1.5)	5.15dd(10.0,2.0)	5.19dd(10.0,2.0)	5.19dd(10.0,2.0)	5.31dd(10.0,2.0)
	5.22dd(17.0,1.5)	5.22dd(17.0,2.0)	5.28dd(17.0,2.0)	5.29dd(18.0,2.0)	5.37dd(17.0,2.0)
1′-H	4.71d(7.5)	4.70d(8.0)	4.69d(8.0)	4.70d(8.0)	4.61d(8.0)
2′-H	3.23dd(9.0,7.5)	3.22dd(9.0,8.0)	3.20dd(9.0,8.0)	3.20dd(9.0,8.0)	3.06dd(9.0,8.0)
3′-H	3.39t(9.0)	3.38t(9.0)	3.39t(9.0)	3.38t(9.0)	
4′-H				3.29dd(9.5,9.0)	
5′-H				3.33ddd (9.5,5.5,2.0)	
6′-H	3.69dd(12.0,5.5)	3.68dd(12.0,5.5)	3.68dd(12.0,5.5)	3.68dd(12.0,5.5)	3.65dd(12.0,5.5)
	3.90dd(12.0,1.5)	3.90dd(12.0,2.0)	3.90dd(12.0,2.0)	3.90dd(12.0,2.0)	3.87dd(12.0,2.0)
OMe	—	3.84s	—	3.81s	—
	—	—	—	3.81s	—







303. $R^1 = R^2 = Me$, $R^3 = H$

304. $R^1 = Me$, $R^2 = R^3 = H$

305. $R^1 = R^3 = H$, $R^2 = Me$

306. $R^1 = R^2 = R^3 = H$

307. $R^1 = Me$, $R^2 = H$

308. $R^1 = H$, $R^2 = Me$

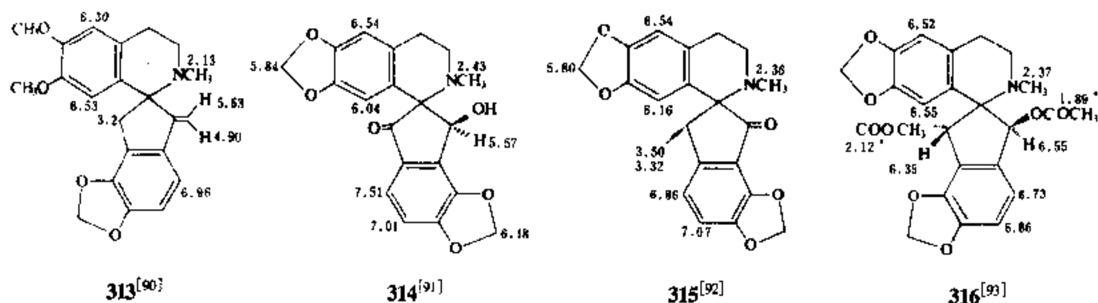
309. $R^1 = R^2 = H$

310. $R^1 = R^2 = Me$

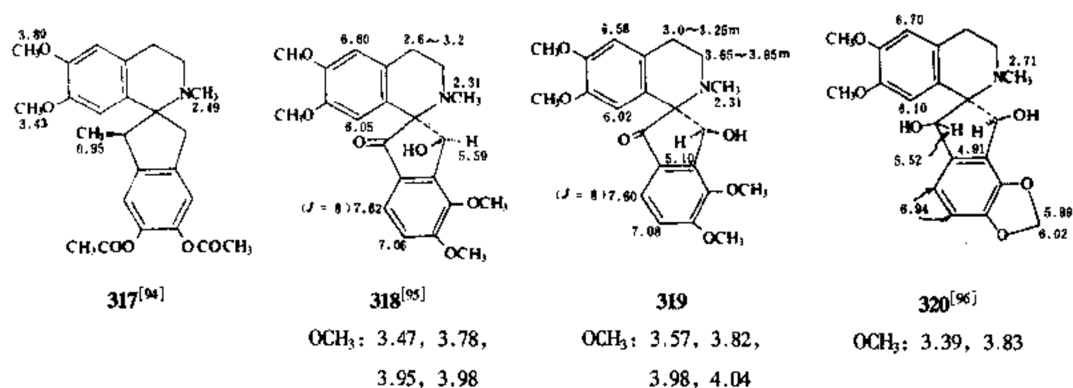
311. $R^1 = R^2 = H$

312. $R^1 = Me$, $R^2 = H$

六、螺环苄基异喹啉生物碱的¹H-NMR化学位移及偶合常数



313[90]　314[91]　315[92]　316[93]

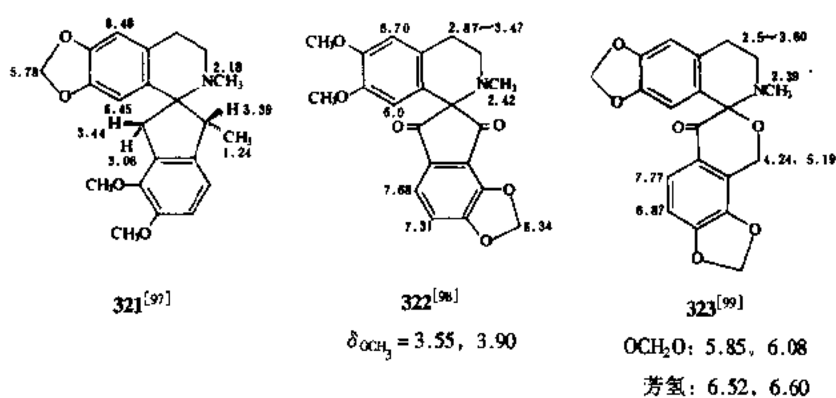


317[94]

318[95]
OCH₃: 3.47, 3.78, 3.95, 3.98

319
OCH₃: 3.57, 3.82, 3.98, 4.04

320[96]
OCH₃: 3.39, 3.83

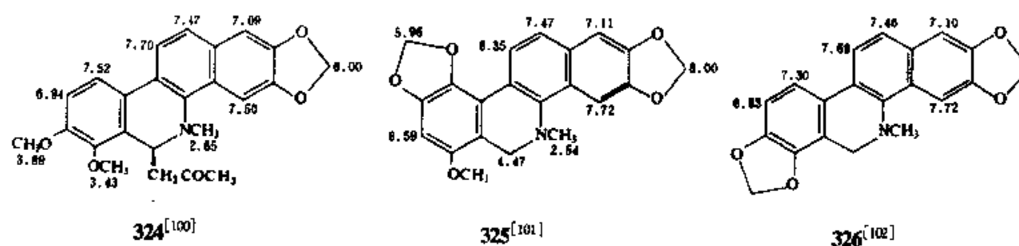


321[97]

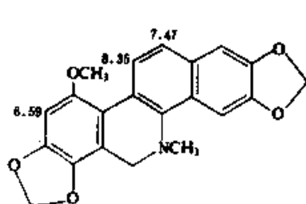
322[98]
δ_{OCH_3} = 3.55, 3.90

323[99]
OCH₂O: 5.85, 6.08
芳氢: 6.52, 6.60

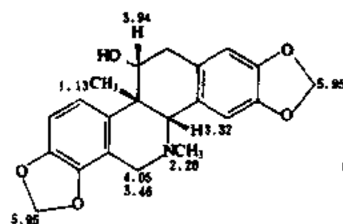
七、苯啡啶生物碱的¹H-NMR化学位移



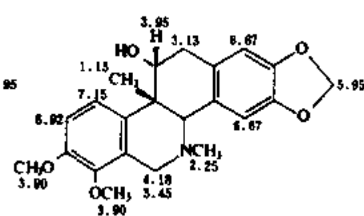
324[100]　325[101]　326[102]



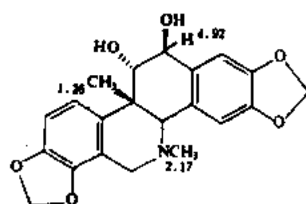
327



328[103]



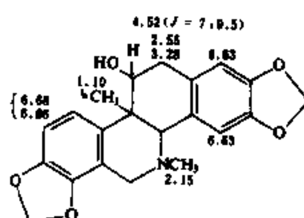
329[103]



330[104]

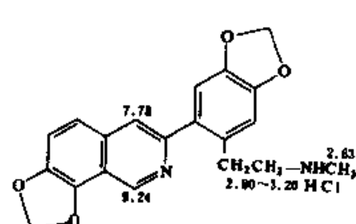
O—CH₂—O: 5.96, 5.98

芳氢: 6.65~7.10



331

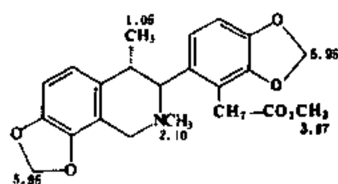
O—CH₂O: 5.92, 5.95



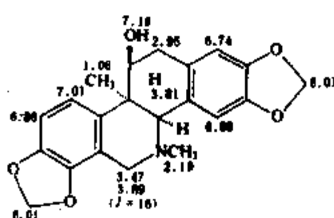
332[105]

O—CH₂—O: 6.10, 6.38

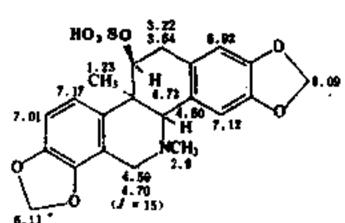
芳氢: 6.77, 7.00, 7.49, 7.63
($J=9$)



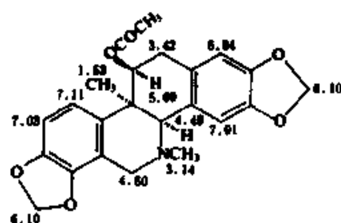
333



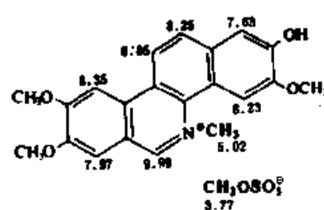
334[106]



335



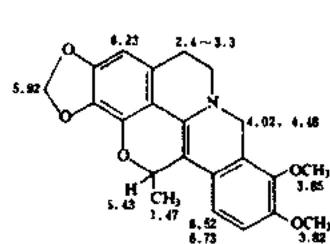
336

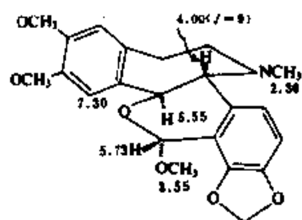


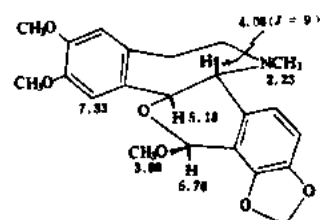
337[107]

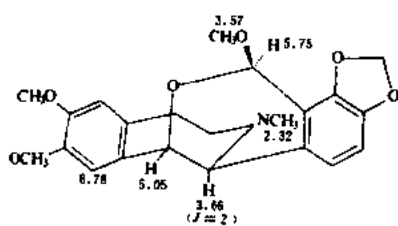
OCH_3: 4.08, 4.15, 4.26

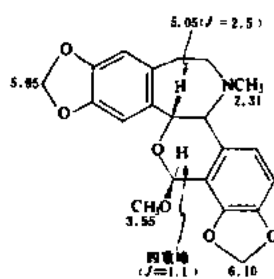
八、苯酞异喹啉生物碱的¹H-NMR 化学位移及偶合常数

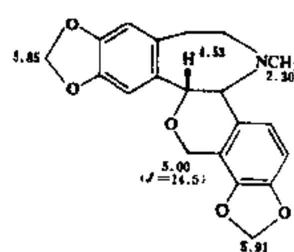

338[108]

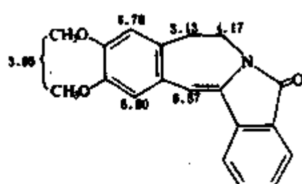

339[109]

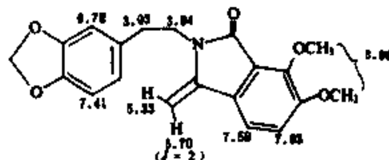

340[110]

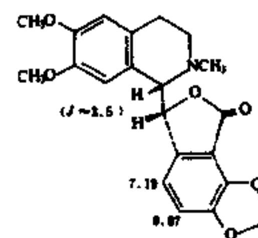

341

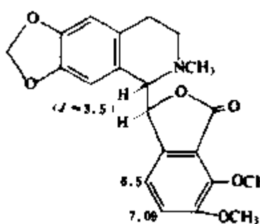

342[111]

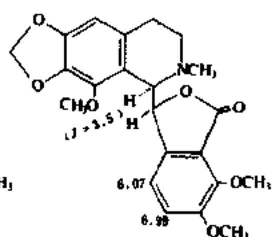

343

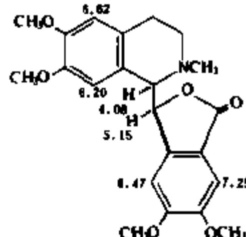

344[112]

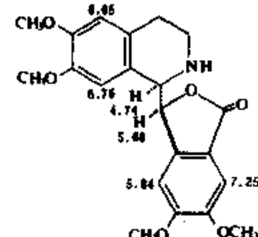

345

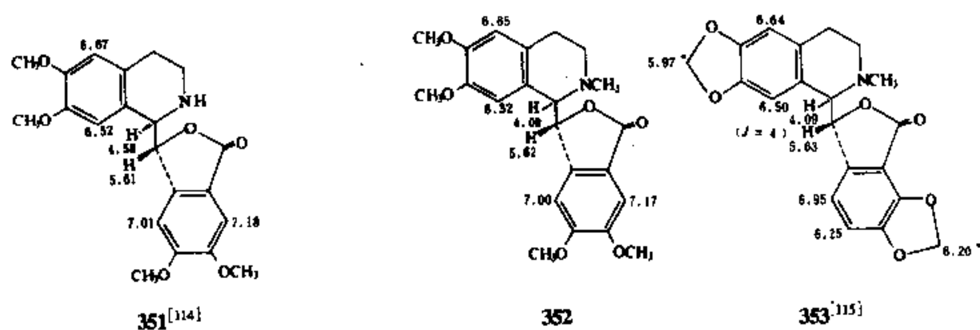

346[113]


347

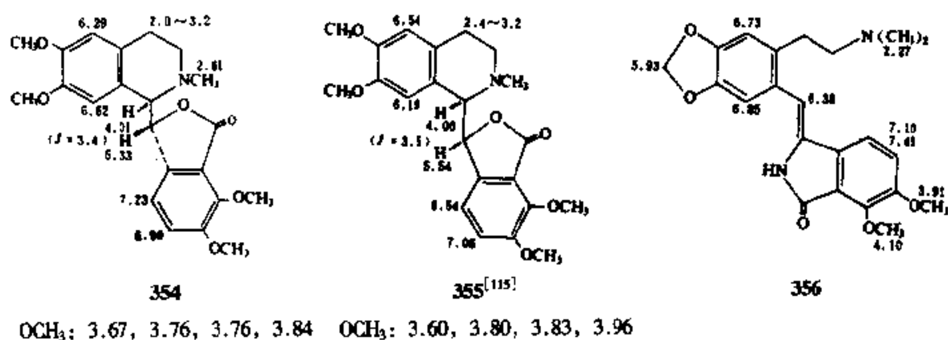

348


349[114]


350[114]



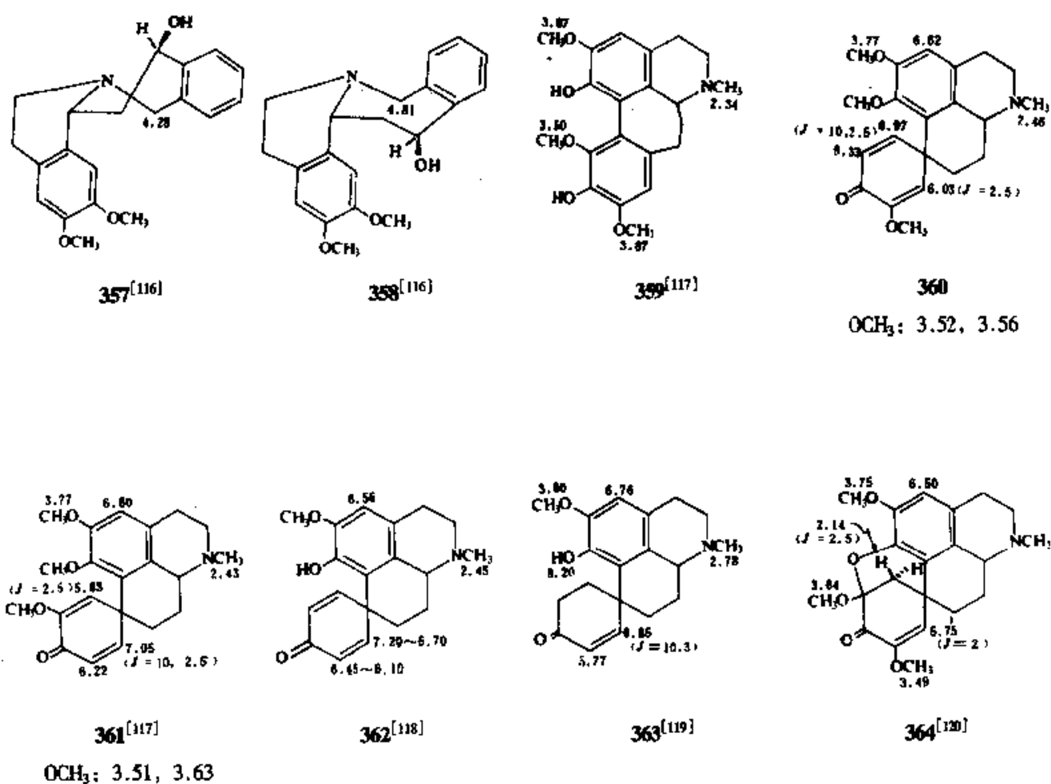
351[114]　　352　　353[115]



354　　355[115]　　356

OCH_3: 3.67, 3.76, 3.76, 3.84　OCH_3: 3.60, 3.80, 3.83, 3.96

九、其他异喹啉生物碱的^{1}H-NMR化学位移及偶合常数

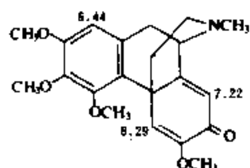


357[116]　　358[116]　　359[117]　　360

OCH_3: 3.52, 3.56

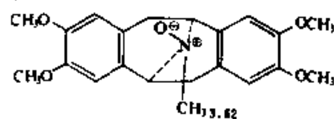
361[117]　　362[118]　　363[119]　　364[120]

OCH_3: 3.51, 3.63



365[121]

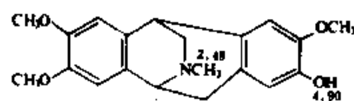
OCH_3：3.78，3.82，3.82，3.98



366[122]

OCH_3：3.80，3.85，4.22，4.28

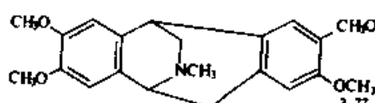
芳氢：6.68，6.79，7.36，7.36



367[123]

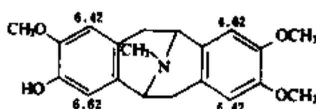
OCH_3：3.86

芳氢：6.75，(2H)，6.61，6.54

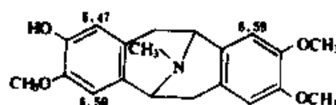


368

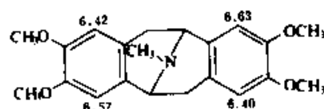
OCH_3：3.86



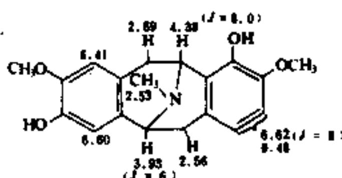
369[124]



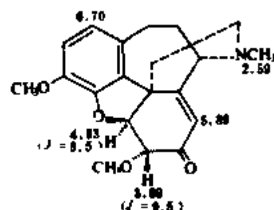
370



371[124]

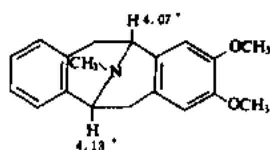


372[124]



373[125]

OCH_3：3.62，3.86



374[126]

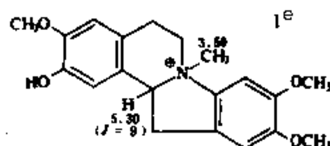
NCH_3：2.56

OCH_3：3.79，3.87

芳氢：7.26～7.00（4H）

6.67，6.49

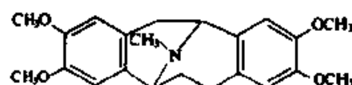
—CH_2—：2.92～2.47，m（2H），3.69～3.32，m（2H）



375[127]

OCH_3：3.78，3.84

芳氢：6.73，6.81，7.07，7.55



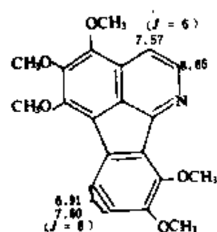
376

N—CH_3：2.53

OCH_3：3.85，3.85，3.90，3.90

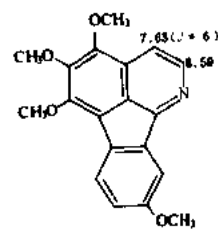
芳氢：6.67～6.5

—CH_2—：4.23～2.37（8H）



377

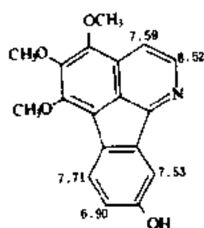
OCH_3：3.94，4.02，4.08，4.10，4.17



378[128]

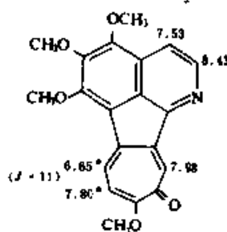
OCH_3：3.94，4.05，4.11，4.13

芳氢：7.82，7.68，6.96



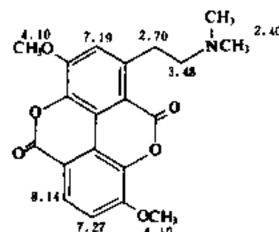
379

OCH_3：4.04，4.08，4.10

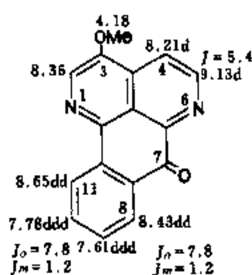


380[128]

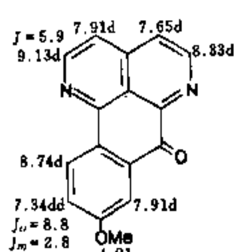
OCH_3：3.92，4.04，4.10，4.14



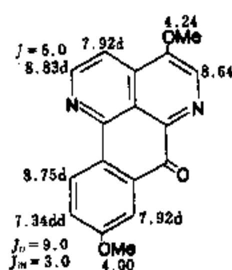
381[129]



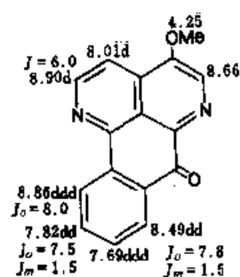
382[401]



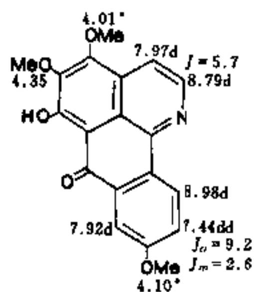
383[402]



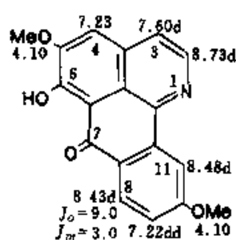
384[402]



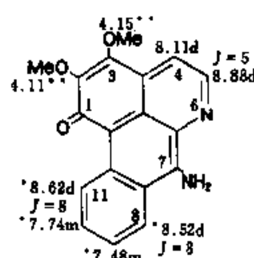
385[402]



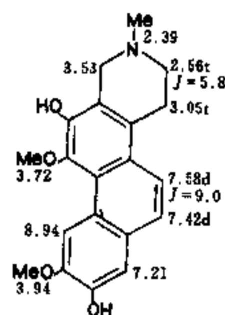
386[403]



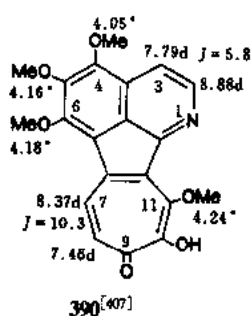
387[404]



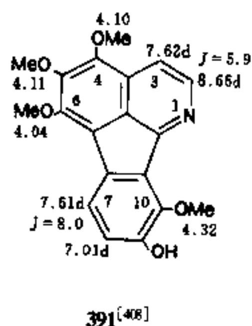
388[405]



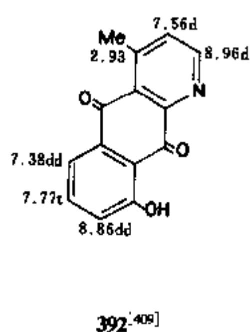
389[406]



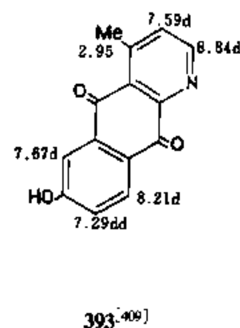
390[407]



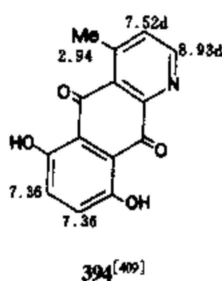
391[408]



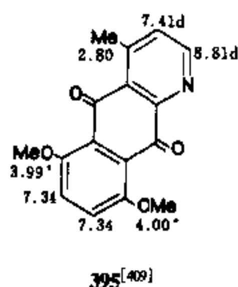
392[409]



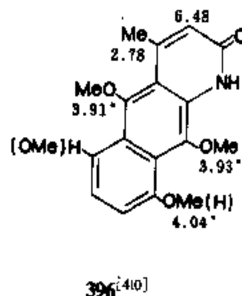
393[409]



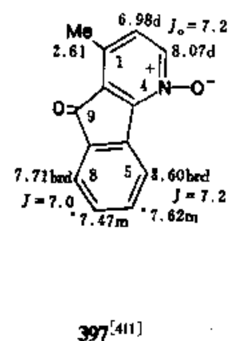
394[409]



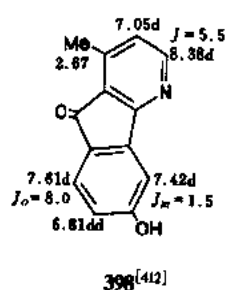
395[409]



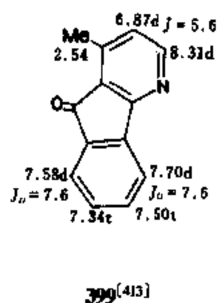
396[410]



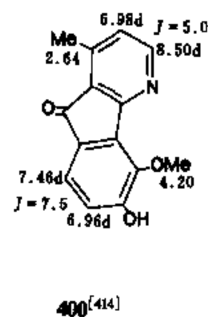
397[411]



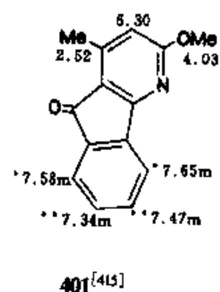
398[412]



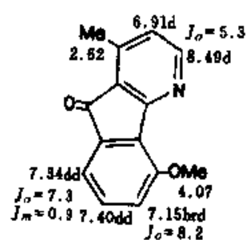
399[413]



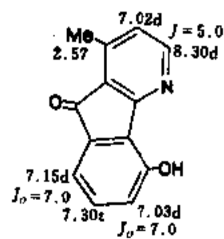
400[414]



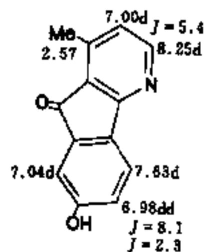
401[415]



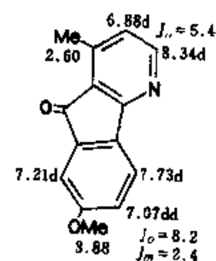
402[377]



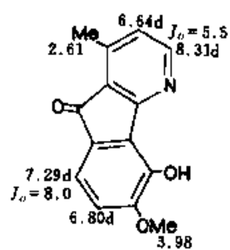
403[412]



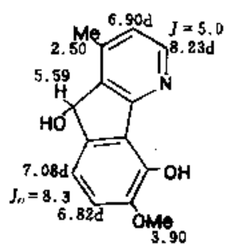
404[412]



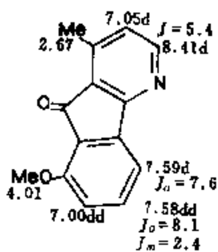
405[412]



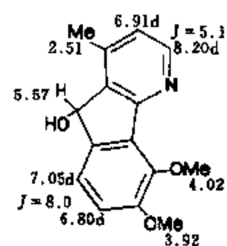
406[414]



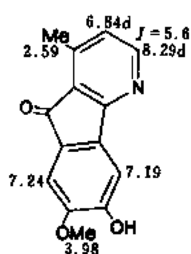
407[377]



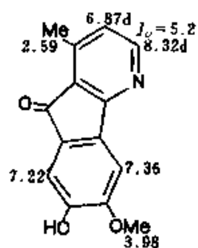
408[412]



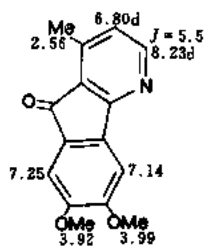
409[377]



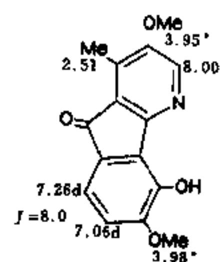
410[416]



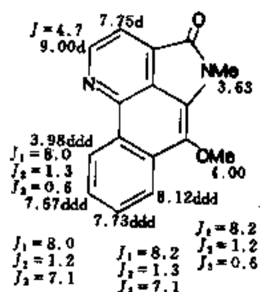
411[417]



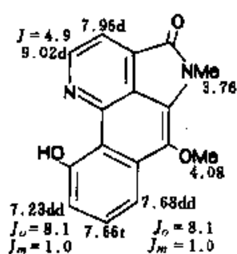
412[416]



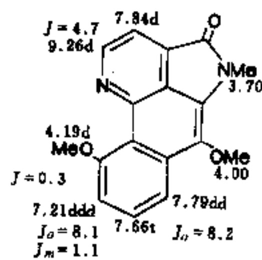
413[418]



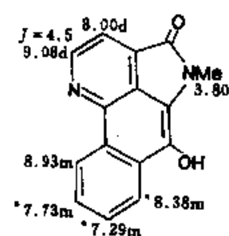
414[419]



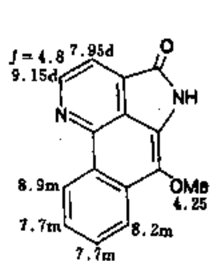
415[419]



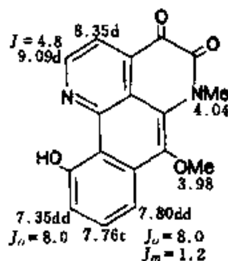
416[419]



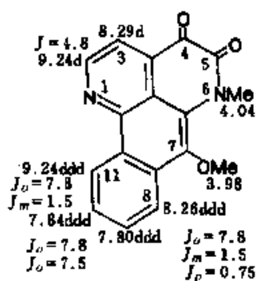
417[420]



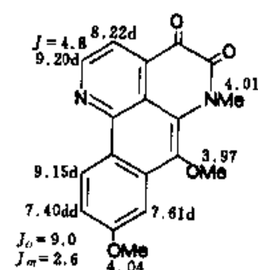
418[421]



419[402]

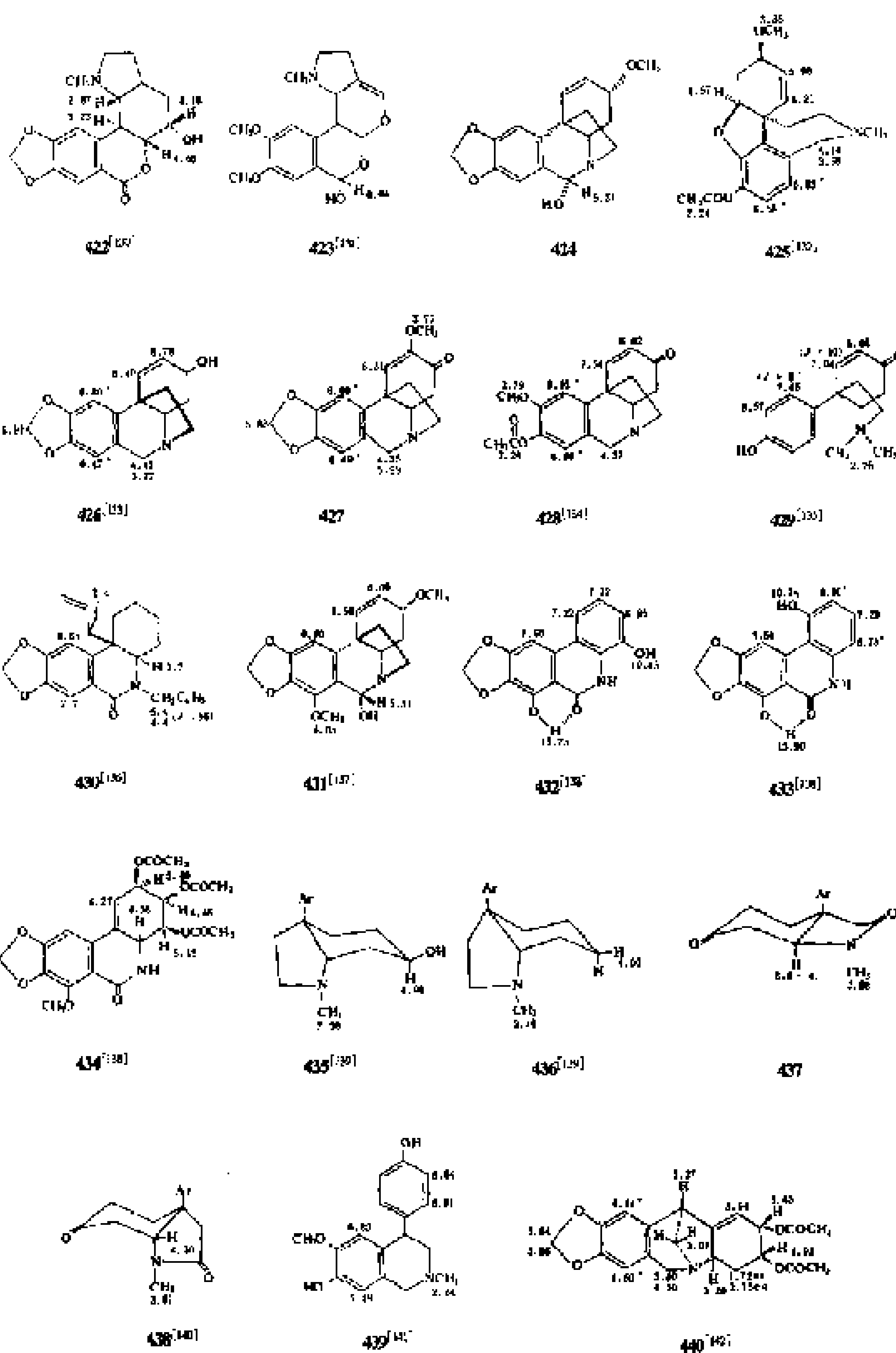


420[402]



421[402]

十、石蒜生物碱的¹H-NMR化学位移及偶合常数



441[143]

442[143]

十一、刺桐生物碱的^{1}H-NMR化学位移及偶合常数

443[144]

OCH_3: 3.43 (6H), 3.21, 3.02

444[145]

445[146]

446[146]

447[146]

448[147]

449[147]

450[147]

451[148]

OCH_3: 3.72, 3.62

452[148]

OCH_3: 3.74, 3.64

453[148]

OCH_3: 3.92, 3.87 (6H)

454[149]

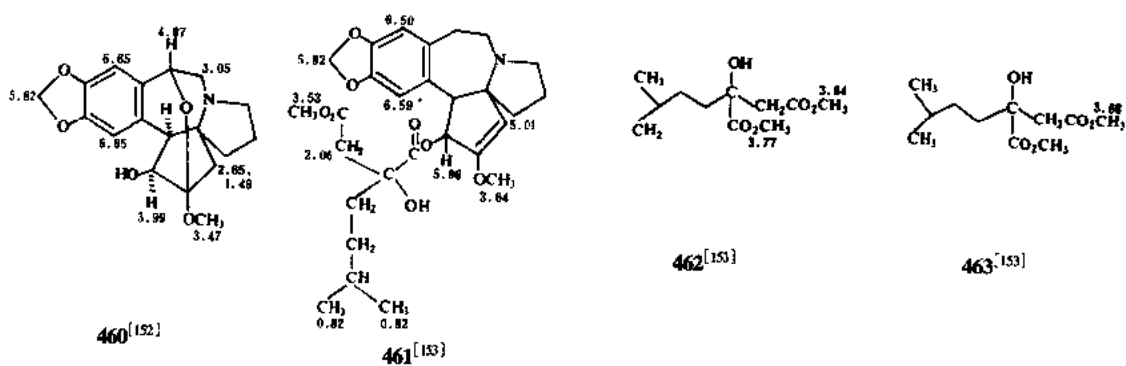
455[149]

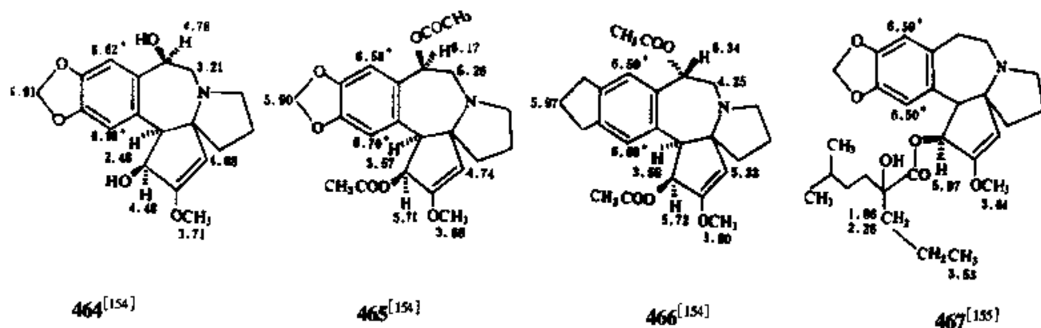
456[150]

457[150]

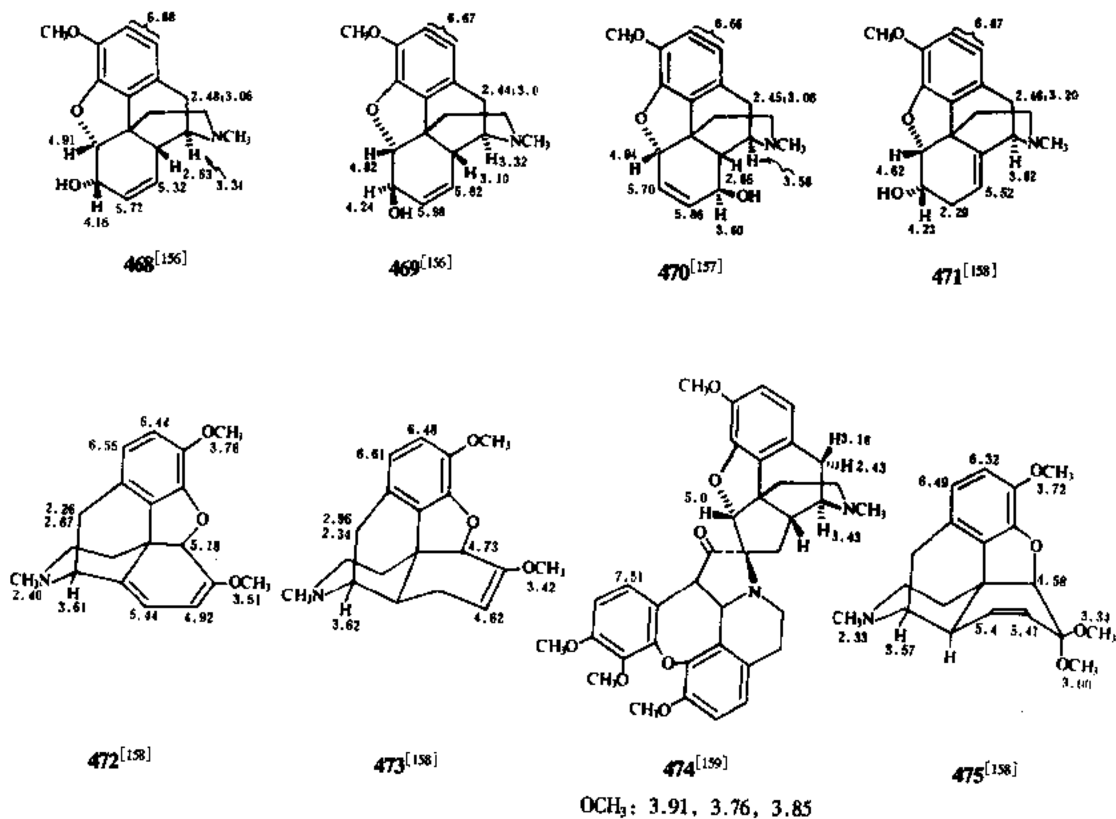
458[151]

459[152]

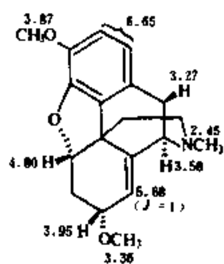


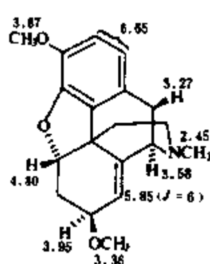


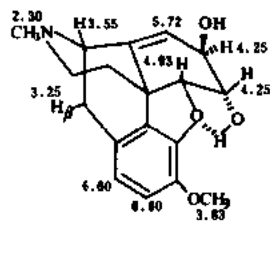
十二、吗啡生物碱的^{1}H-NMR化学位移及偶合常数

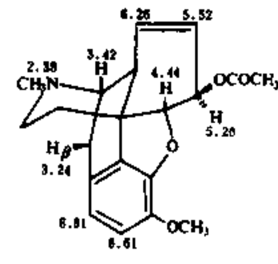


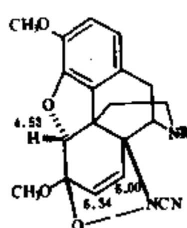
OCH$_3$：3.91，3.76，3.85

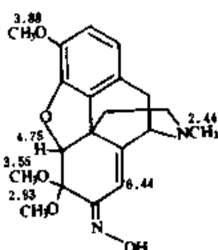

476[160]

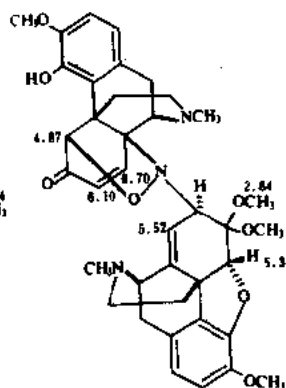

477[160]


478[161]


479[162]

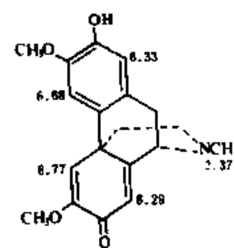

480[163]


481[164]

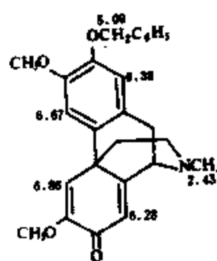

482[165]

NCH_3: 2.50, 2.41

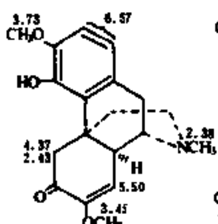
OCH_3: 3.86, 3.77, 3.56

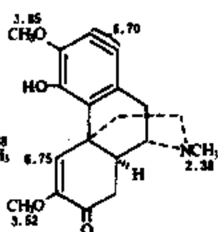

483[166]

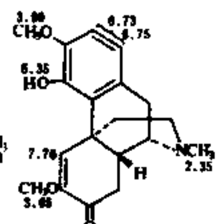
OCH_3: 3.79, 3.89

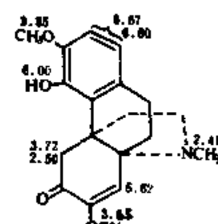

484[167]

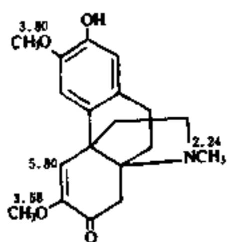
OCH_3: 3.80, 3.88

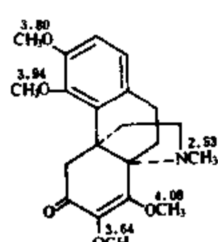

485[168]

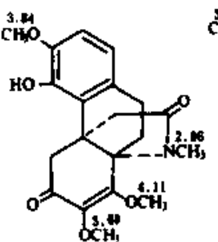

486[168]

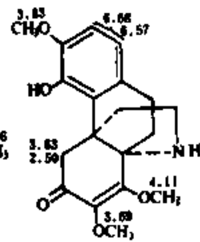

487[169]

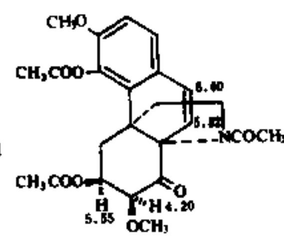

488[170]

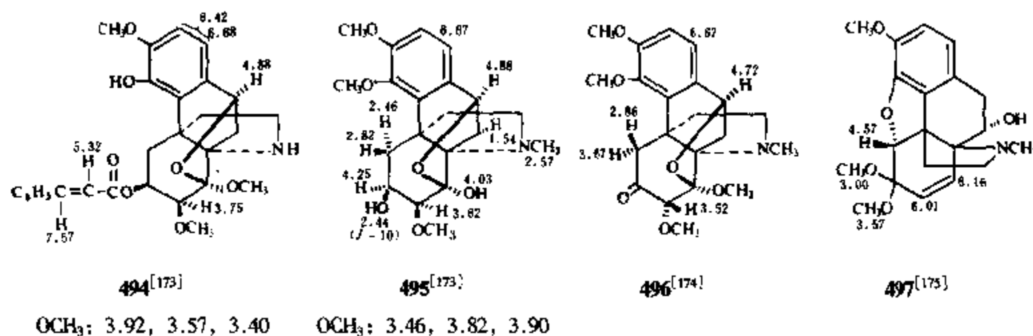

489[171]


490[172]


491[172]

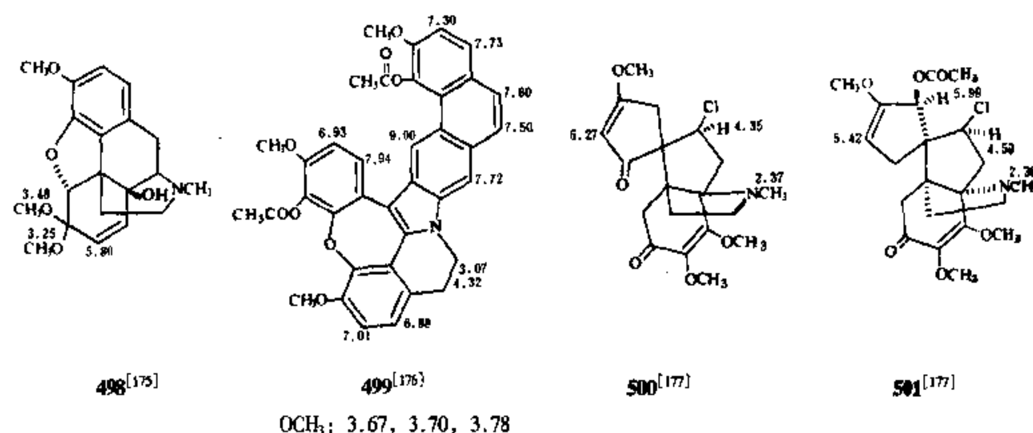

492[172]


493[173]



494[173] 495[173] 496[174] 497[175]

OCH_3: 3.92, 3.57, 3.40　OCH_3: 3.46, 3.82, 3.90

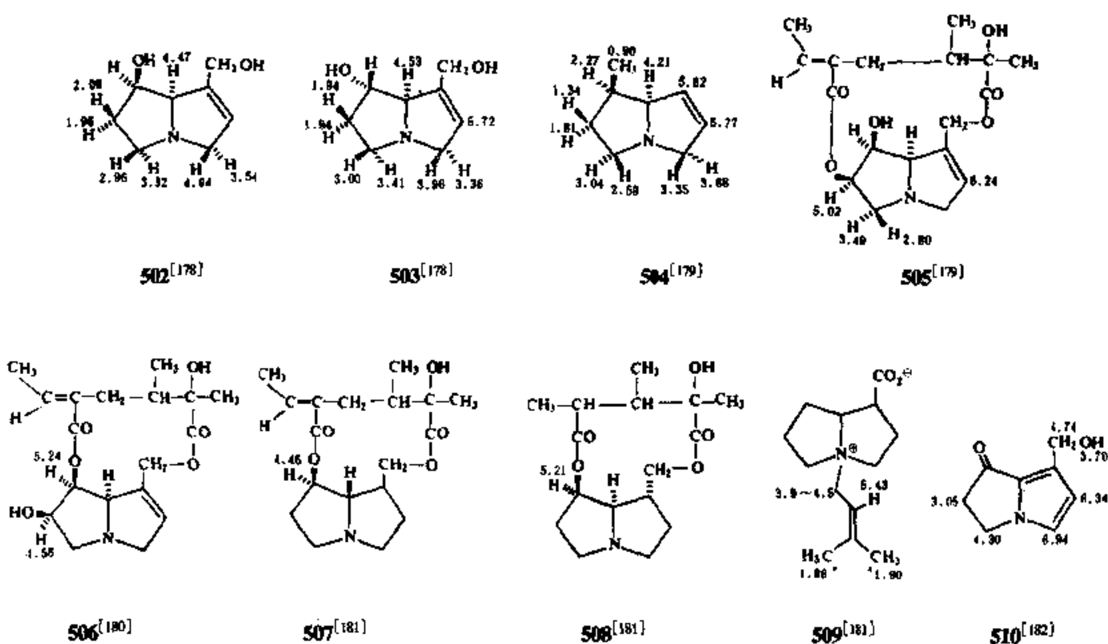


498[175] 499[176] 500[177] 501[177]

OCH_3: 3.67, 3.70, 3.78

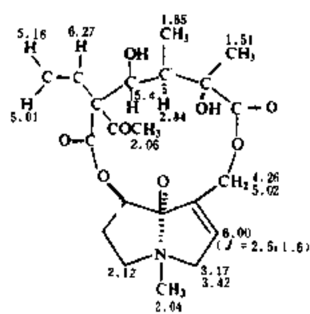
第二节　吡咯里西啶、吲哚里西啶及喹诺里西啶生物碱的^{1}H-NMR 化学位移及偶合常数

一、吡咯里西啶生物碱的^{1}H-NMR 化学位移

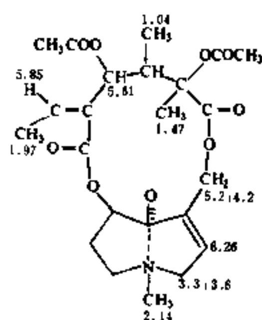


502[178] 503[178] 504[179] 505[179]

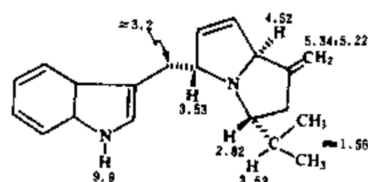
506[180] 507[181] 508[181] 509[181] 510[182]



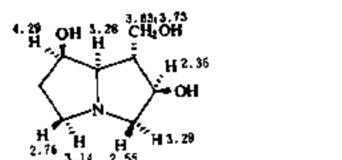
511 (a)[183]



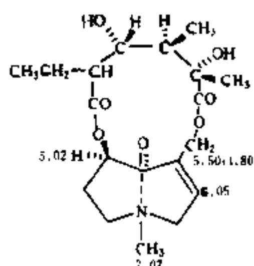
511 (b)[184]



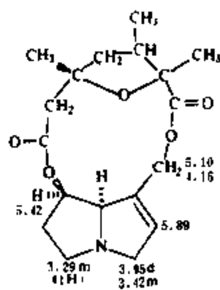
512[185]



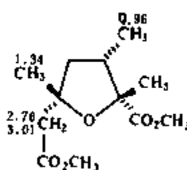
513[186]



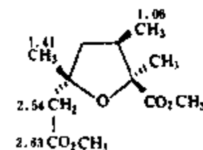
514[186]



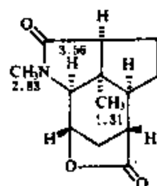
515[186]



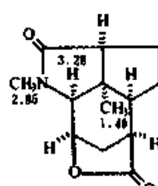
516[187]



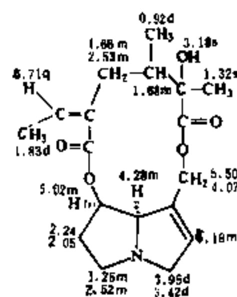
517[187]



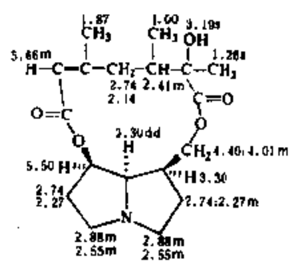
518[188]



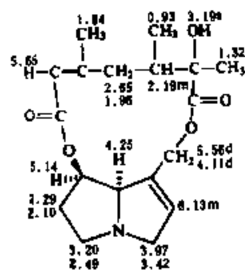
519[188]



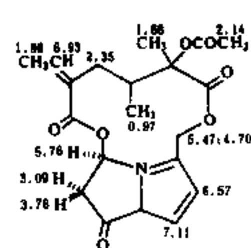
520[189]



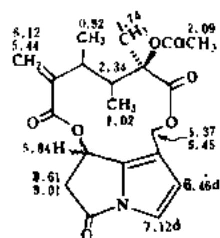
521[190]



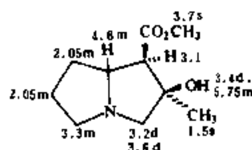
522[190]



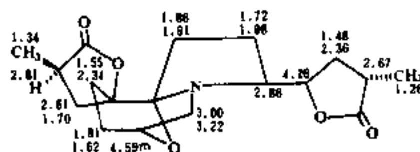
523[191]



524[192]

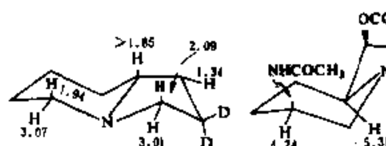


525[192]

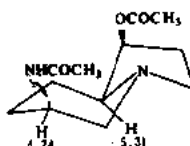


526[193]

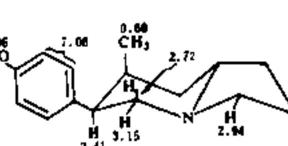
二、吲哚里西啶生物碱的^{1}H-NMR化学位移



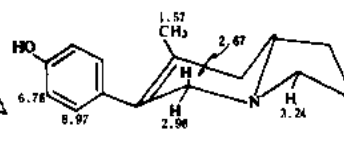
527[194]



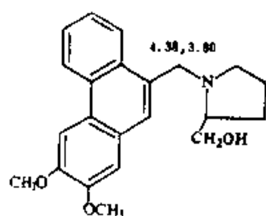
528[194]



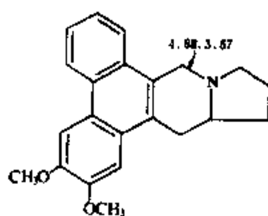
529[195]



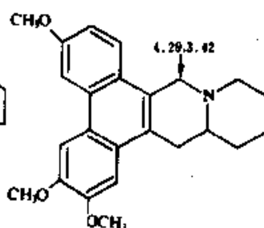
530[196]



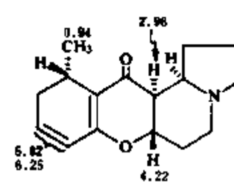
531[197]



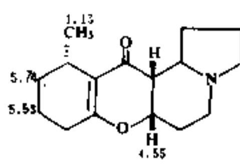
532[197]



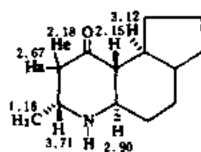
533[198]



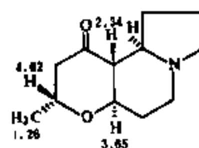
534[199]



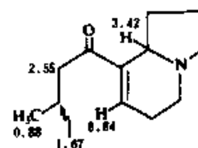
535[199]



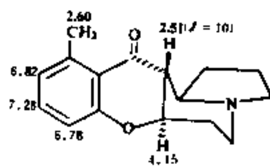
536[200]



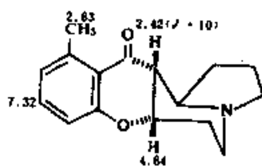
537[200]



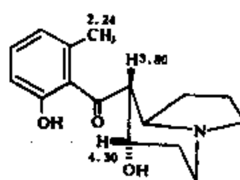
538[200]



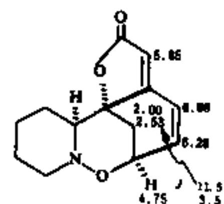
539[201]



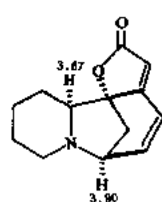
540[201]



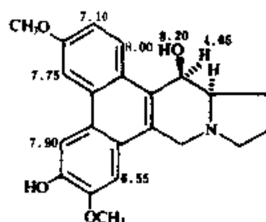
541[202]



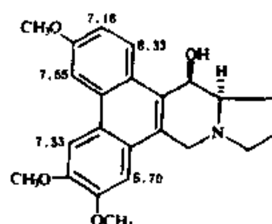
542[203]



543[203]

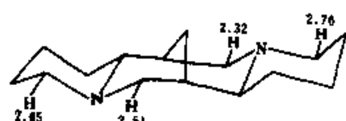


544[204]

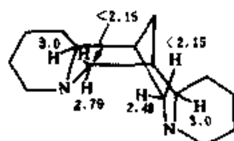


545[204]

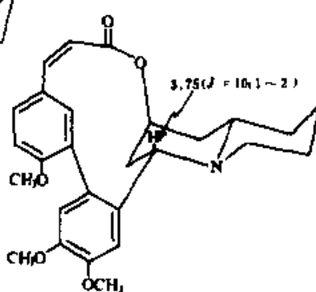
三、喹诺里西啶生物碱的^{1}H-NMR 化学位移及偶合常数



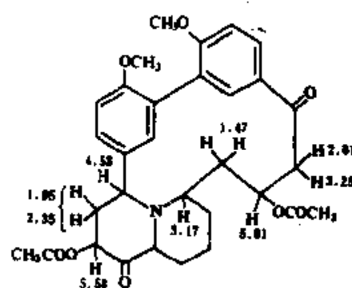
546[205]



547[205]



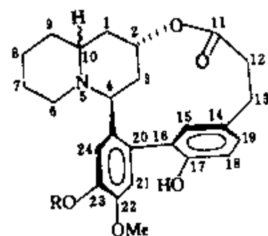
548[206]



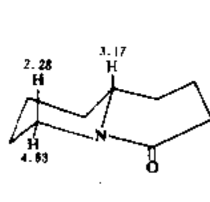
549[207]

表 6-2 喹诺里西啶生物碱 550 和 551 的^{1}H-NMR 化学位移和偶合常数[422]

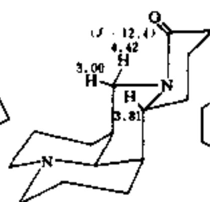
质子 \ 化合物	550			551		
	δ_H	$^2J,^3J$	^4J	δ_H	$^2J,^3J$	nOe
1a-H	1.72brt	1e,10a		1.67m	1e,2e,10	
1e-H	1.75brd	1a,2e	3e	2.27m	1a,2e,10	
2e-H	5.34m	1e,3a,3e		5.36brm	1a,3a,3e	
3a-H	2.03td	2e,3e,4a		2.06m	2e,3e,4a	24-H
3e-H	2.24brd	2e,3a,4a		2.27brd	2e,3a,4a	15-H
4a-H	3.61dd(10,1.1Hz)	3a,3e		4.56d(11.1Hz)	3a,3e	15-H,9a
6a-H	1.14m	6e,7a		2.47td	6e,7a,7e	
6e-H	2.69	6a	8e	2.90brd	6a,7a,7e	24-H
7a-H	1.40	6a,7e,8a		0.57tt	6a,7e	
7e-H	1.48	7a		0.83d	7a,6e	
8a-H	1.18	7a,8e,9e		1.11m	7e,8e	
8e-H	1.61	8a,9a,9e		1.28m	8a	
9a-H	1.27～1.30dd	8a,9e,10a		1.58	10,9e	4a
9e-H	1.40～1.43m	8a,8e,9a,10a		1.42	9a,10	
10-H	1.96brt	1a,9a,9e		3.21b	1a,1e,9a,9e	
12-H	5.87d(12.5)	13		5.86d(12.5Hz)	13	
13-H	6.79d(12.5)	12		6.80d(12.5Hz)	12	
15-H	7.12d(2.2)	19	13	7.15d(2.1Hz)	19	4a,3e
18-H	7.00d(8.3)	19		7.01d(8.29Hz)	19	
19-H	7.19dd(8.3,2.2)	18,15	13	7.21dd(8.29,2.1Hz)	15,18	
21-H	6.93s			6.96s		OMe
24-H	7.18s		4a	7.23s		6e,3a
22-OMe	3.90s			3.91s		21-H



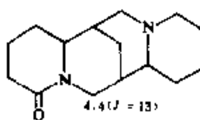
	10-H	12～13	R
550.	α	CH＝CH	H
551.	β	CH＝CH	H



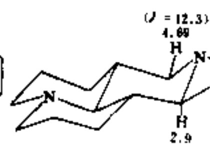
552[208]



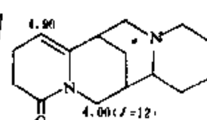
553[208]



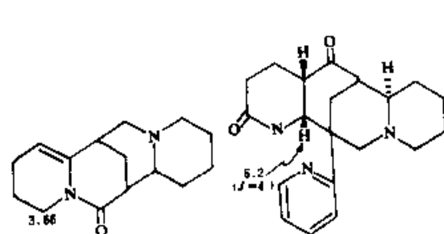
554[209]



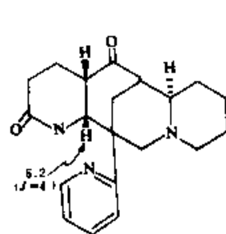
555[209]



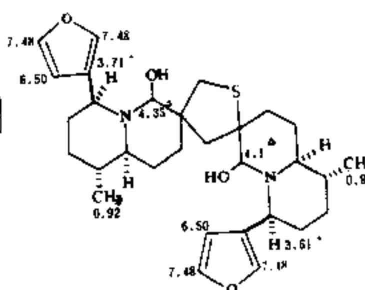
556[209]



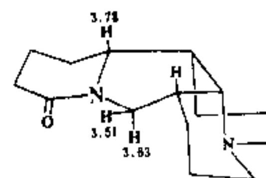
557[209]



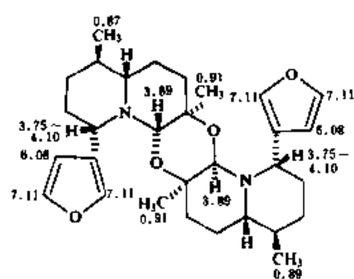
558[210]



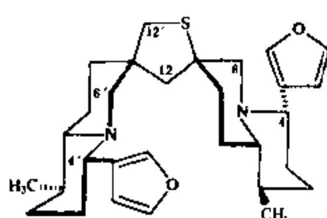
559[211]



560[212]



561[213]



563[215]

$\delta_{6'a\text{-}H} = 1.40$ $(J_{6'a,6'e} = -11.5)$

$\delta_{6a\text{-}H} = 1.92$ $(J_{6a,6e} = -11.5)$

$\delta_{6e\text{-}H} = 3.11$ $(J_{6a,6e} = -11.5)$

$(J_{6e,8e} = 2)$

$\delta_{6'e\text{-}H} = 3.17$

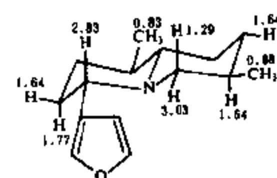
$\delta_{4a\text{-}H} = 2.80$

$(J_{4a,3a} = 10.5)$

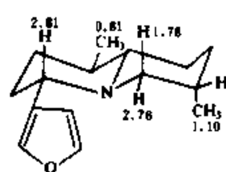
$(J_{4a,3e} = 3.5)$

$\delta_{12a,e\text{-}H} = 2.18$ $(J = -14.0)$

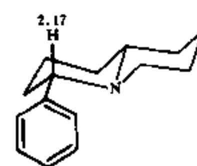
$\delta_{12'a,e\text{-}H} = 2.31$ $(J = -11.5)$



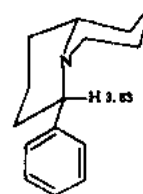
564[215]



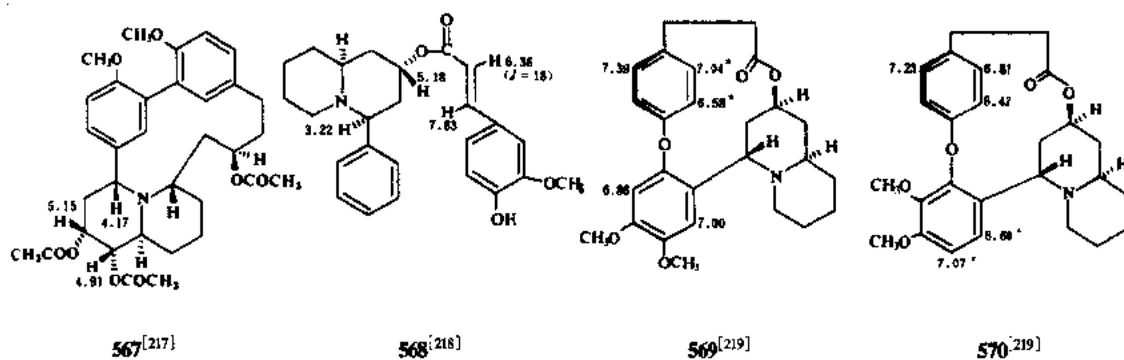
562[214]



565[216]

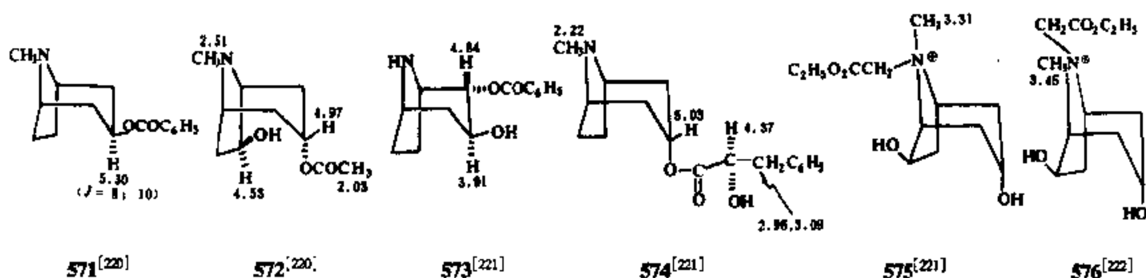


566[216]

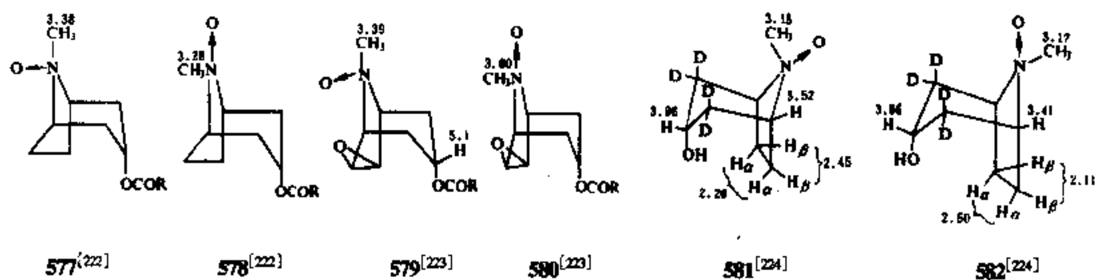


567[217]　568[218]　569[219]　570[219]

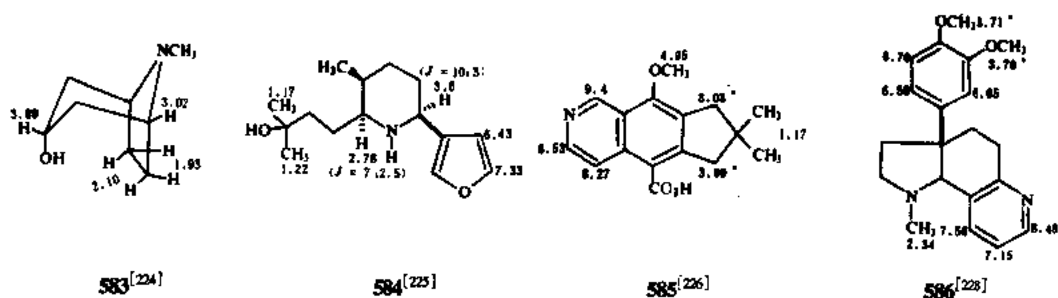
第三节　吡啶及六氢吡啶生物碱的¹H-NMR 化学位移及偶合常数



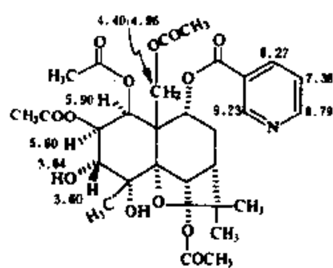
571[220]　572[220]　573[221]　574[221]　575[221]　576[222]



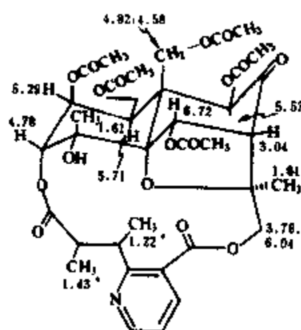
577[222]　578[222]　579[223]　580[223]　581[224]　582[224]



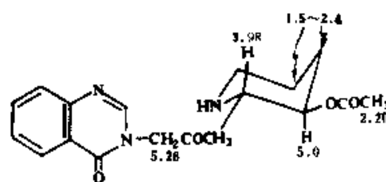
583[224]　584[225]　585[226]　586[228]



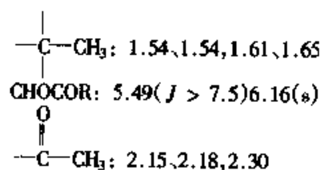
587[227]



588[229]



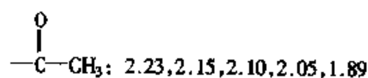
589[230]



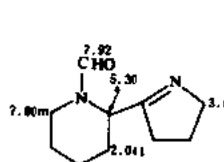
—C—CH3: 1.54、1.54, 1.61、1.65

CHOCOR: 5.49(J > 7.5) 6.16(s)

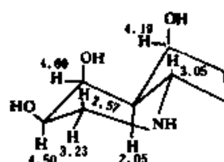
—C(=O)—CH3: 2.15、2.18, 2.30



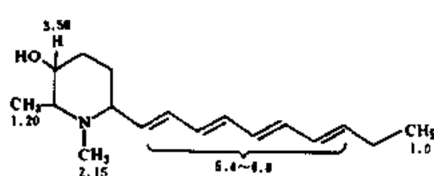
—C(=O)—CH3: 2.23, 2.15, 2.10, 2.05, 1.89



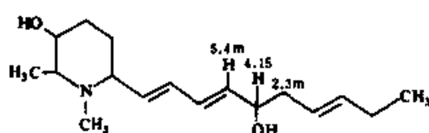
590[231]



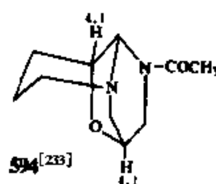
591[232]



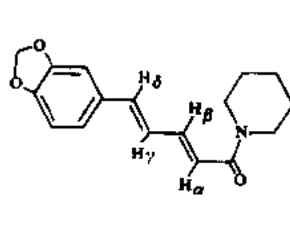
592[232]



593[232]



594[233]

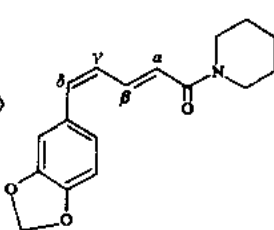


595[234]

$J_{\alpha\beta} = 15.2$

$J_{\beta\gamma} = 11.5$

$J_{\gamma\delta} = 15.8$

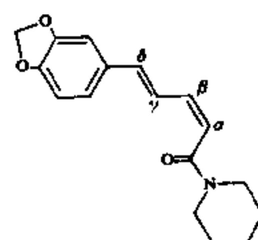


596[234]

$J_{\alpha\beta} = 15.0$

$J_{\beta\gamma} = 11.5$

$J_{\gamma\delta} = 13.0$

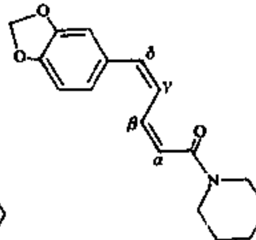


597[234]

$J_{\alpha\beta} = 11.0$

$J_{\beta\gamma} = 11.0$

$J_{\gamma\delta} = 16.3$

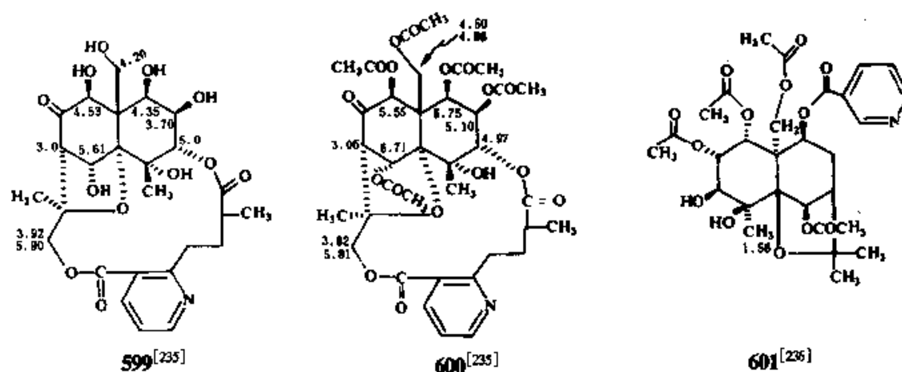


598[234]

$J_{\alpha\beta} = 11.6$

$J_{\beta\gamma} = 11.1$

$J_{\gamma\delta} = 12.6$



599[235]　　600[235]　　601[236]

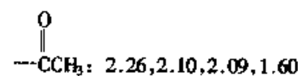
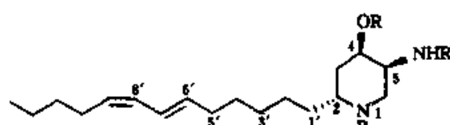
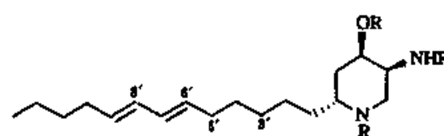


表 6-3　六氢吡啶生物碱 602 和 603 的^{1}H-NMR 化学位移和偶合常数[423]

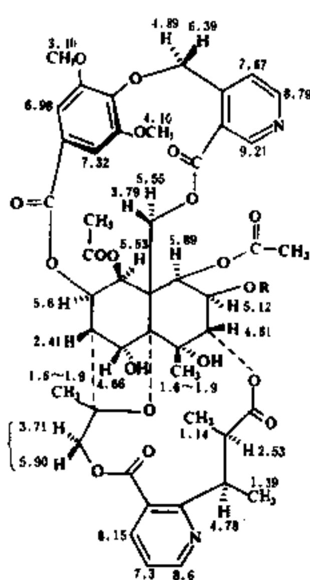
质子＼化合物	602	603	质子＼化合物	602	603
2-H	4.93brs	4.86brs	2'-H_2～4'-H_2	1.20～1.40brs	1.20～1.40brs
2^a-H	4.00brs	3.97brs	5'-H_2	2.07m	2.03m
3-H_2	1.75m	1.74m	6'-H	5.65m	5.46～5.57 m
4-H	5.15m	5.11m	7'-H	6.29dd(15,11)	5.91～5.99 m
5-H	4.31brs	4.34brs	8'-H	5.93t(11)	5.91～5.99 m
5-H	4.51brs	4.47brs	9'-H	5.30m	5.46～5.57 m
6_{ax}-H	3.27brd(14.5)	3.26brd(14.5)	10'-H_2	2.15m	2.03m
6_{ax}-H	2.91brd(14.5)	2.88brd(14.5)	11'-H_2～12'-H_2	1.20～1.40brs	1.20～1.40brs
6_{eq}-H	3.97brd(14.5)	3.87brd(14.5)	13'-H_3	0.89t(7)	0.86t(7)
6_{eq}-H	4.61brd(14.5)	4.58brd(14.5)	—NH—	5.60brs	6.18brd(8)
1'-H_2	1.60m	1.55m	Ac	2.00,2.04,2.06	2.00,2.00,2.01



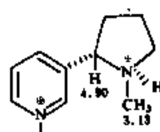
602. R = Ac



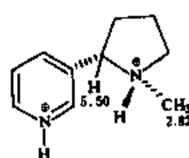
603. R = Ac



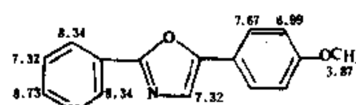
604[237]



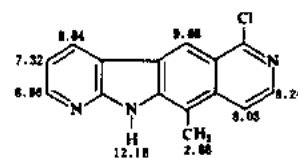
605[238]



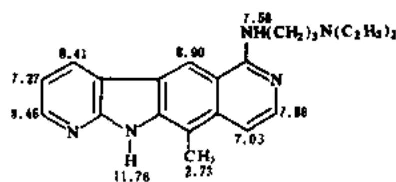
606[238]



607[239]



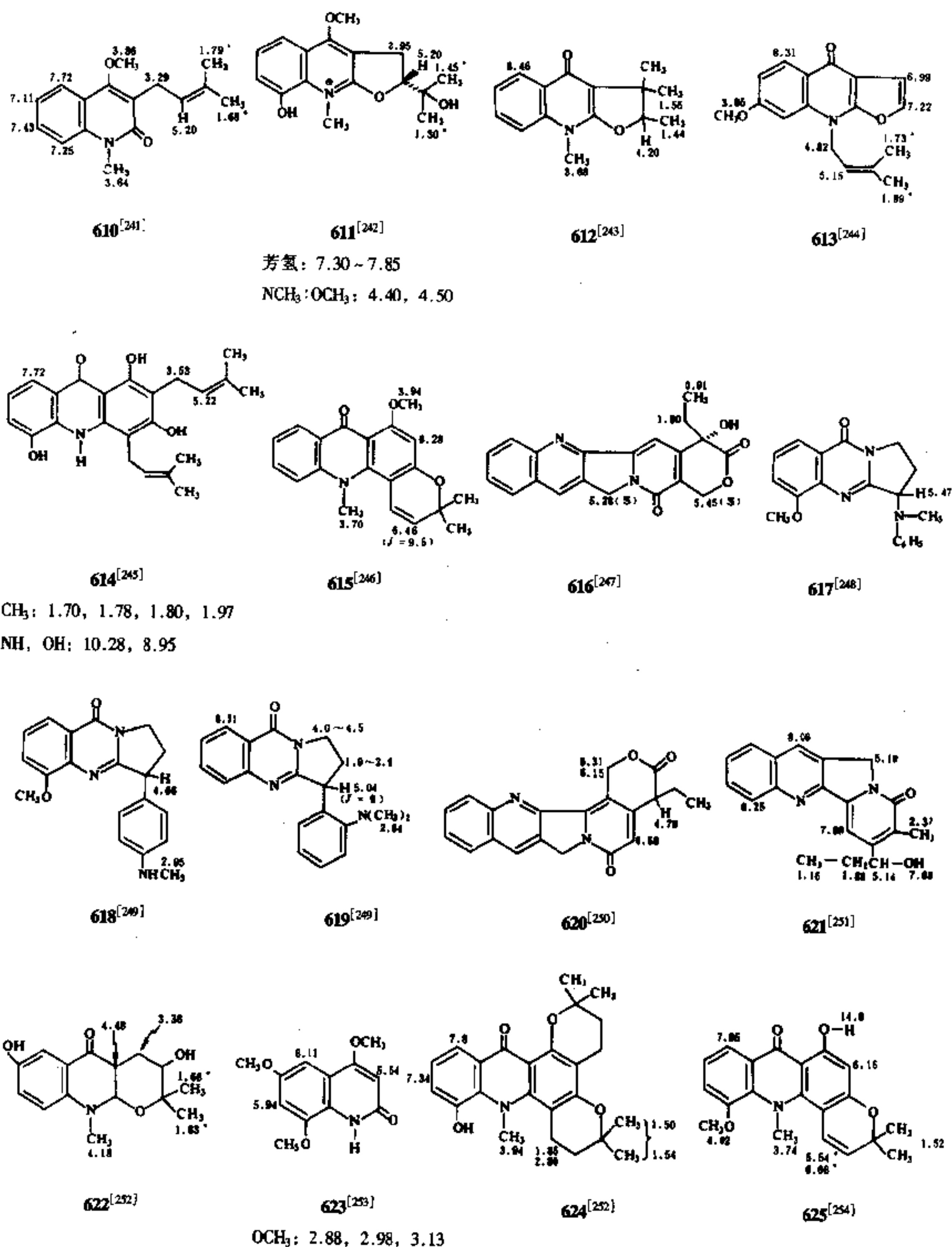
608[240]

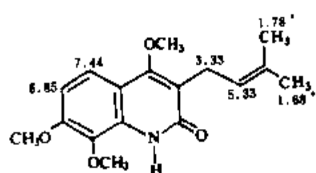


609[240]

第四节　喹啉、喹唑啉、咪唑、胍类生物碱的¹H-NMR 化学位移及偶合常数

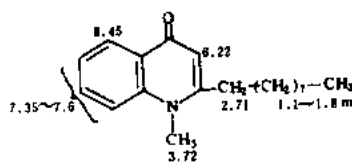
一、喹啉和喹唑啉生物碱的¹H-NMR 化学位移与偶合常数



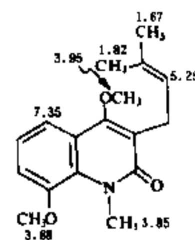


626[255]

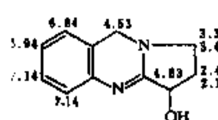
OCH_3：3.90，3.95，3.95



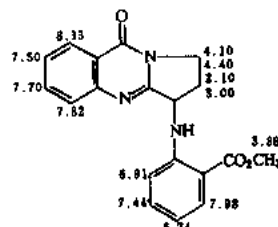
627[256]



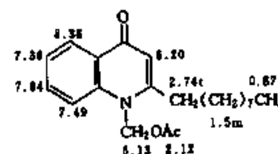
628[257]



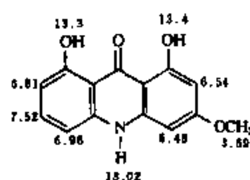
629[424]



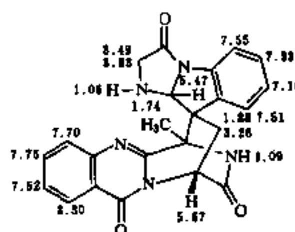
630[424]



631[425]

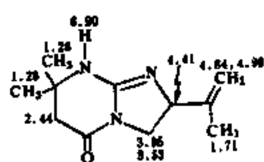


632[425]

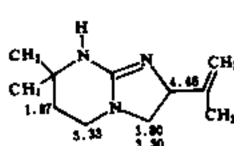


633[426]

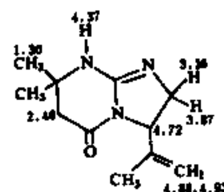
二、咪唑和胍类生物碱的^{1}H-NMR化学位移及偶合常数



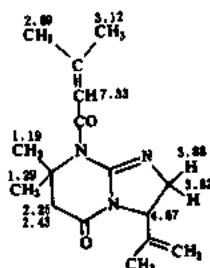
634[258]



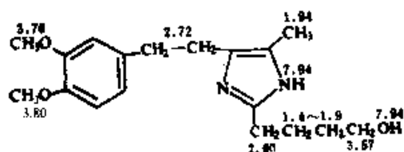
635[258]



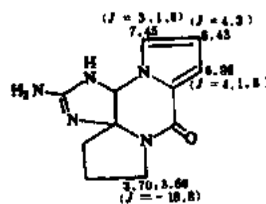
636[258]



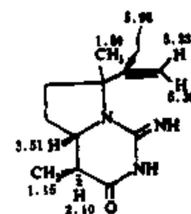
637[258]



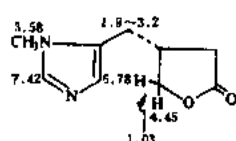
638[259]



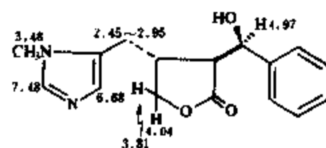
639[260]



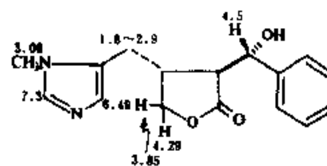
640[261]



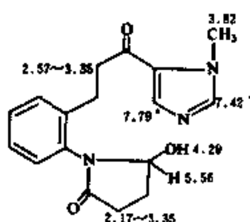
641[262]



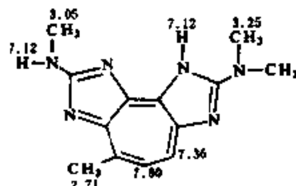
642[262]



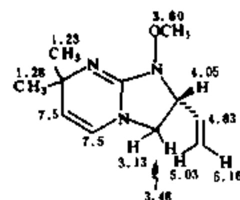
643[262]



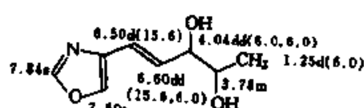
644[263]



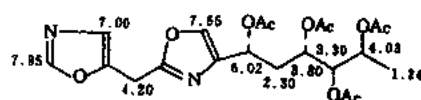
645[264]



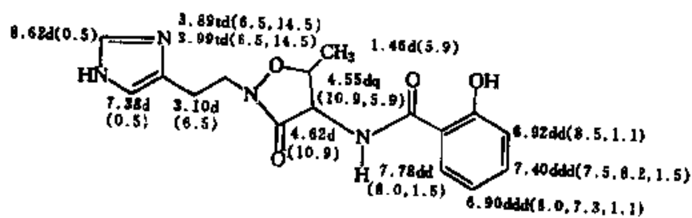
646[265]



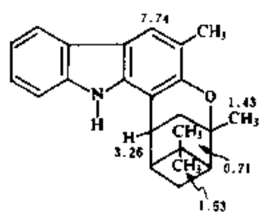
647[427]



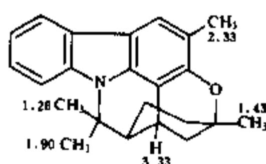
648[428]



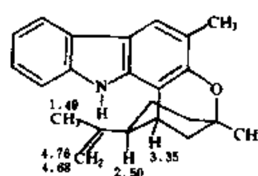
649[429]



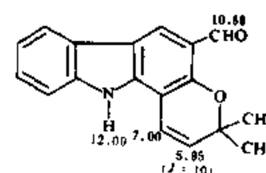
655[268]



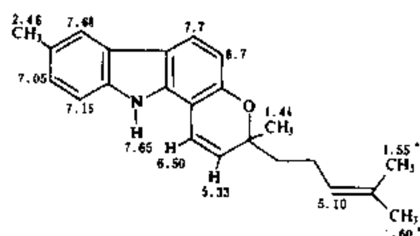
656[268]



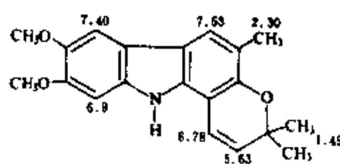
657[269]



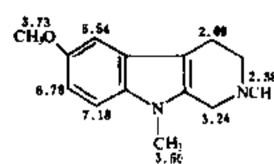
658[270]



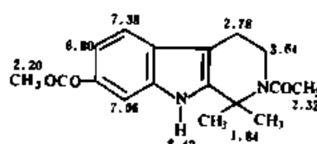
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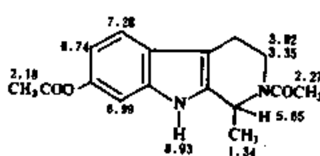
660[271]



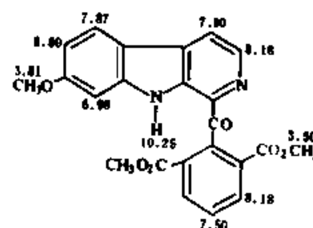
661[272]



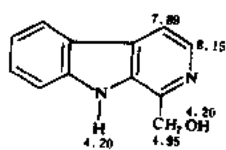
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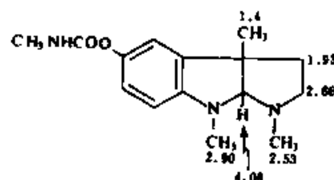
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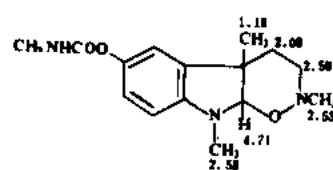
664[274]



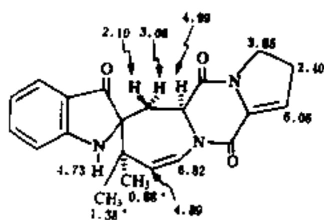
665[275]



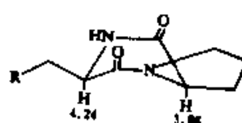
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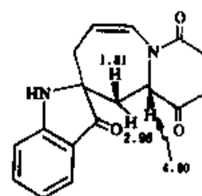
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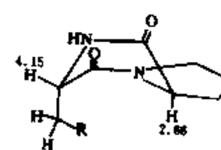
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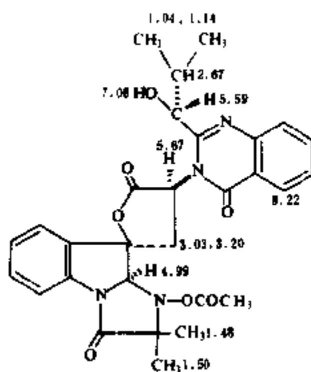
669[279]



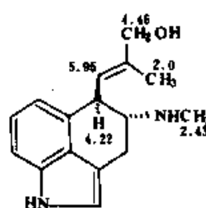
670[278]



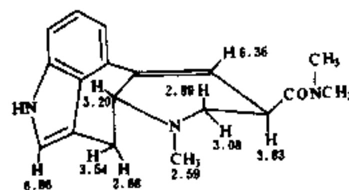
671[279]



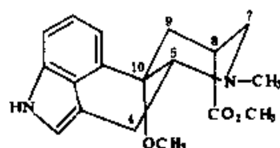
672[280]



673[281]

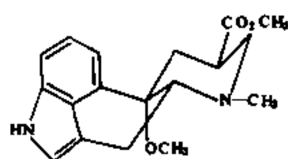


674[282]



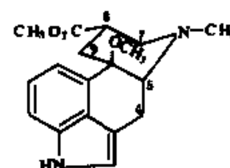
675[283]

7a-H: 2.29
7e-H: 3.59
8e-H: 2.66
9a-H: 1.78
9e-H: 3.58
4a-H: 2.92
4e-H: 3.11
5a-H: 2.25



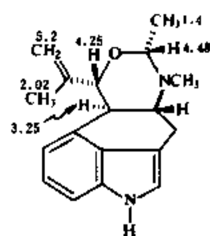
676[283]

7a-H: 2.31
7e-H: 3.31
8a-H: 3.13
9a-H: 1.65
9e-H: 3.24
4a-H: 3.02
4e-H: 3.19
5a-H: 2.35

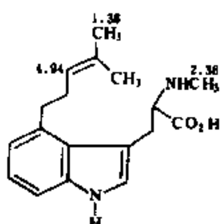


677[284]

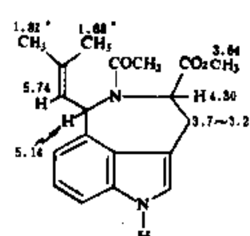
7a-H: 2.81
7e-H: 2.97
8a-H: 3.37
9a-H: 1.86
9e-H: 2.17
4a-H: 3.07
4e-H: 3.12
5e-H: 3.54



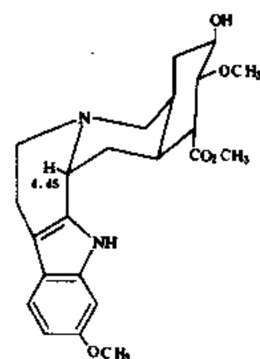
678[284]



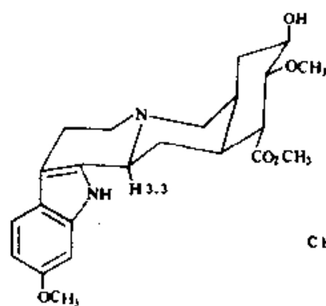
679[284]



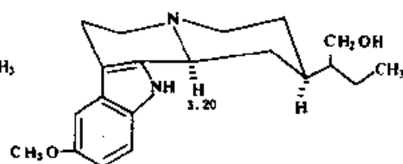
680[284]



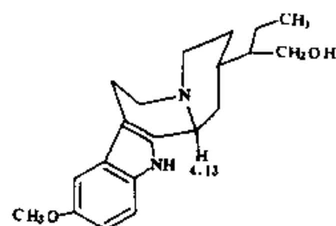
681[285]



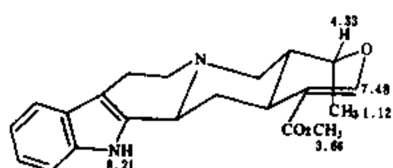
682[285]



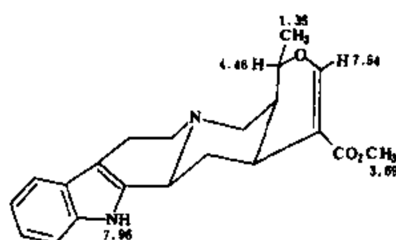
683[286]



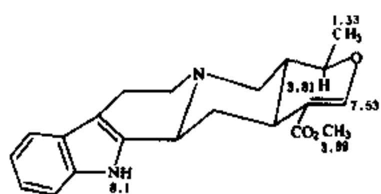
684[286]



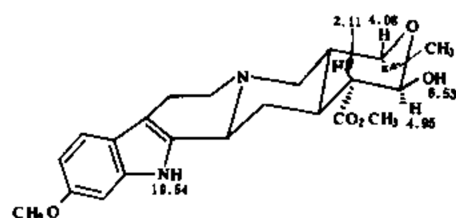
685[286]



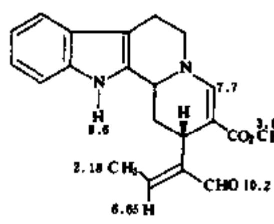
687[287]



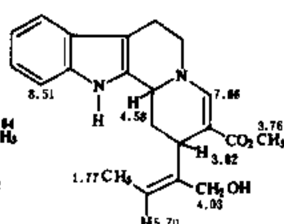
686[286]



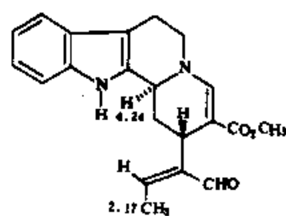
688[288]



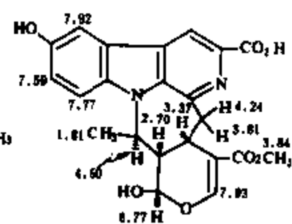
689[289]



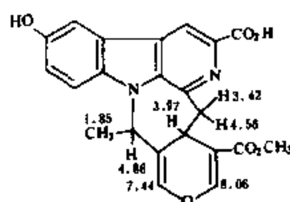
690[290]



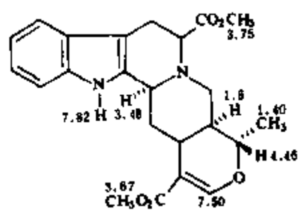
691[290]



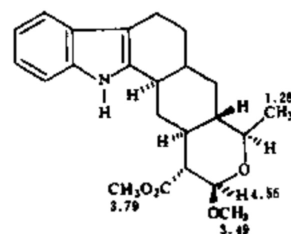
692[290]



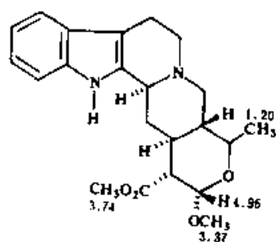
693[291]



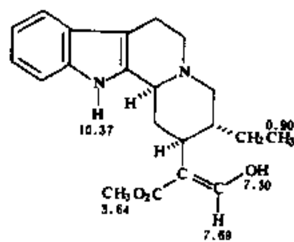
694[292]



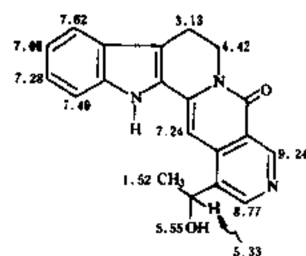
695[292]



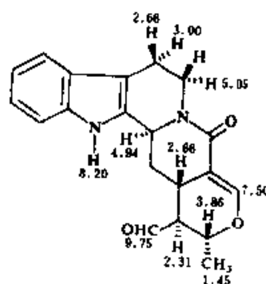
696[293]



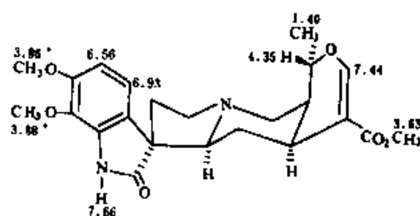
697[294]



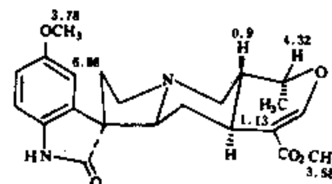
698[295]



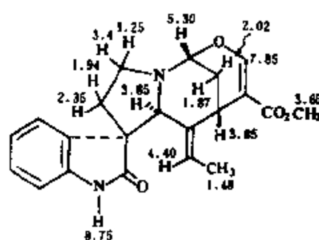
699[296]



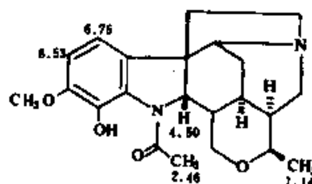
700[297]



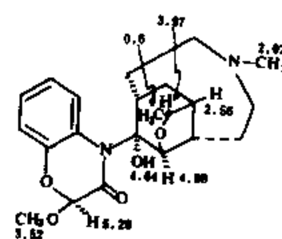
701[298]



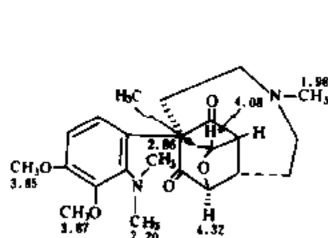
702[299]



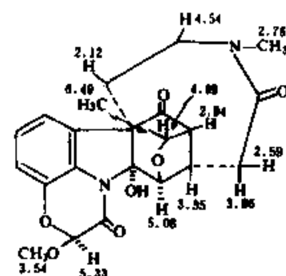
703[300]



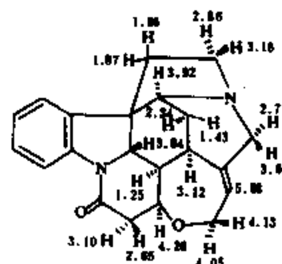
704[301]



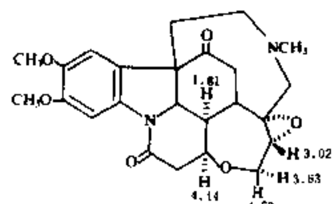
705[301]



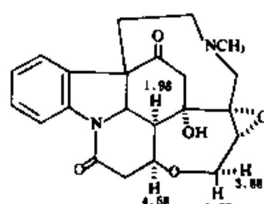
706[301]



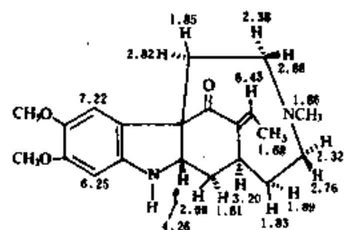
707[302]



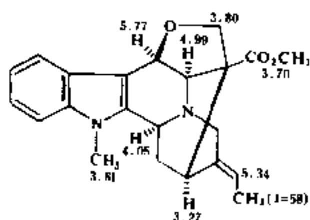
708[303]



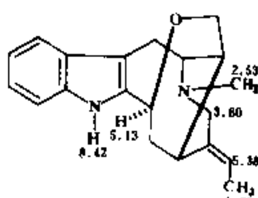
709[303]



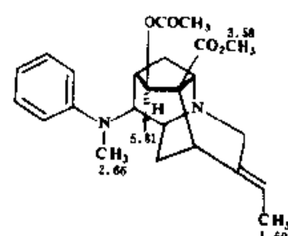
710[304]



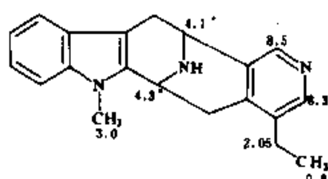
711[305]



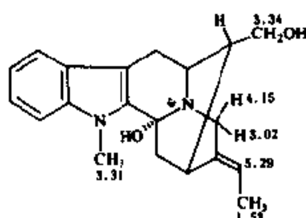
712[306]



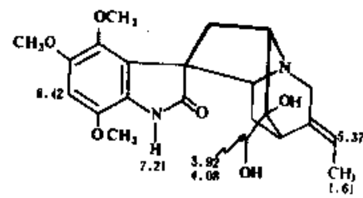
713[307]



714[308]

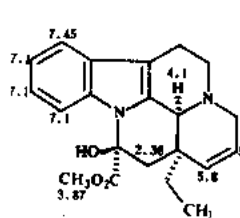


715[309]

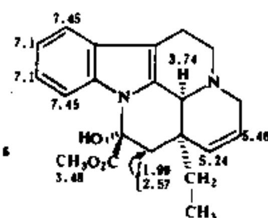


716[310]

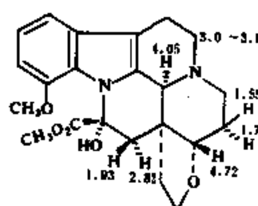
OCH_3: 3.73, 3.80, 3.80



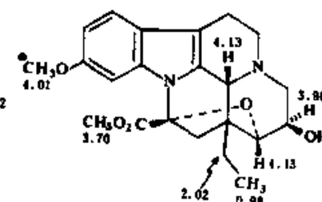
717[311]



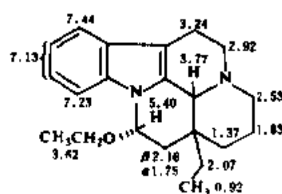
718[311]



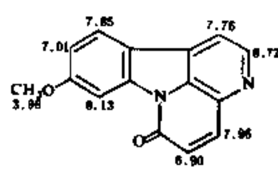
719[312]



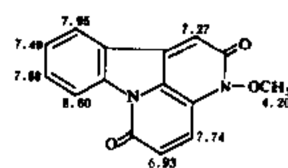
720[313]



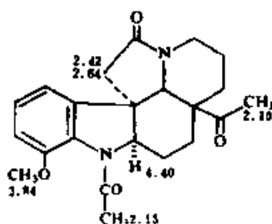
721[314]



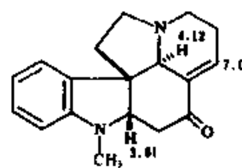
722[315]



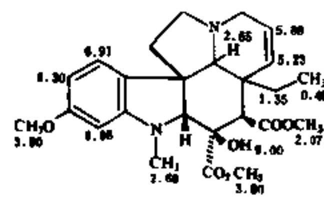
723[315]



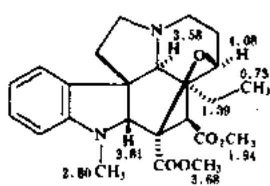
724[316]



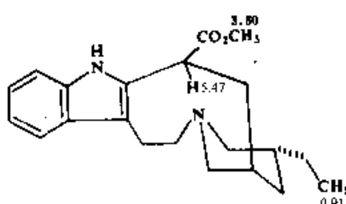
725[317]



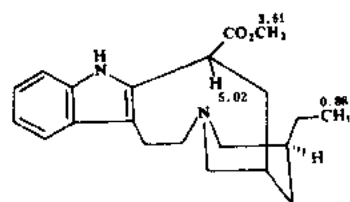
726[318]



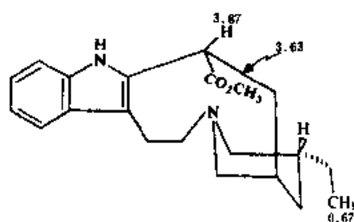
727[319]



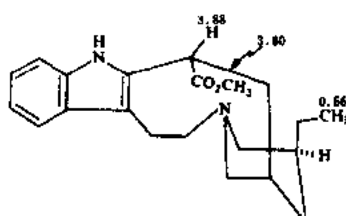
728[320]



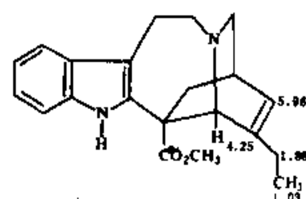
729[320]



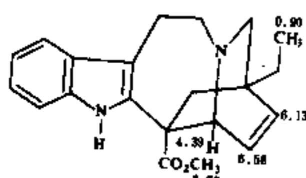
730[320]



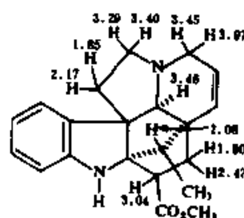
731[320]



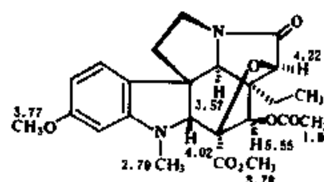
732[321]



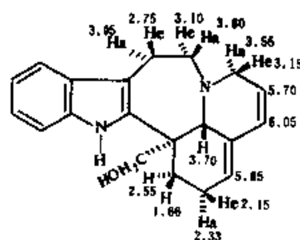
733[322]



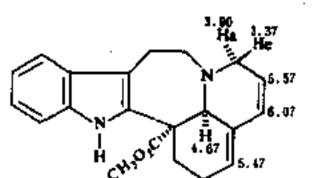
734[323]



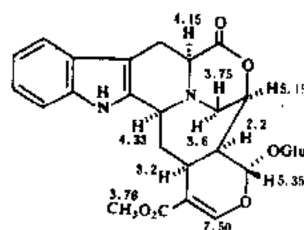
735[323]



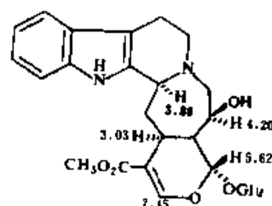
736[324]



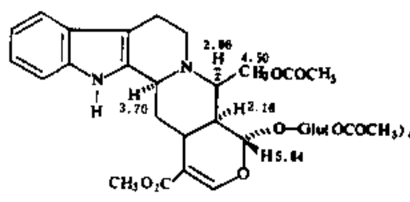
737[325]



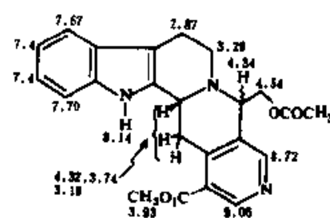
738[326]



739[327]



740[328]



741[329]

742[330]

743[331]

744[332]

745[333]

746[333]

747[334]

748[334]

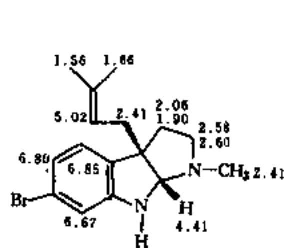
749[334]

750[335]

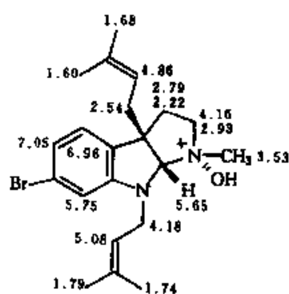
751[336]

752[337]

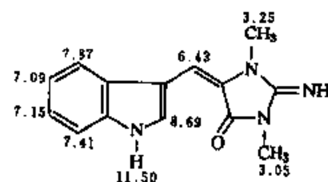
753[337]



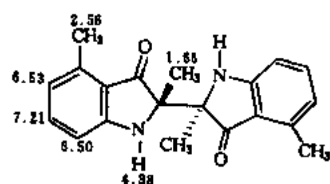
$754^{[430]}$



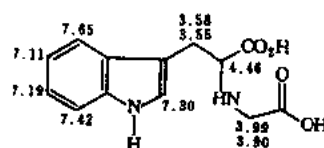
$755^{[431]}$



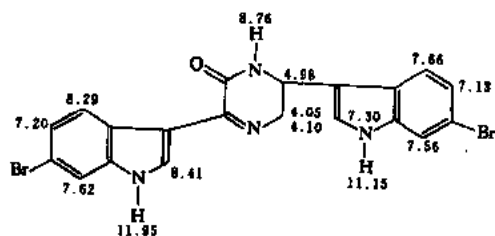
$756^{[432]}$



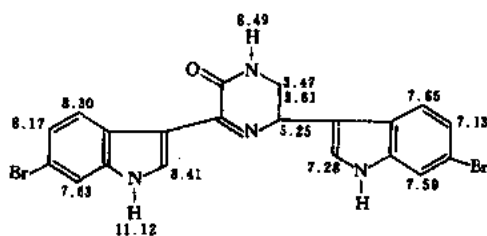
$757^{[433]}$



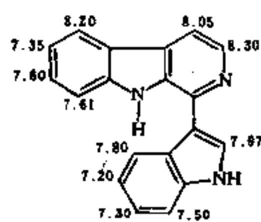
$758^{[434]}$



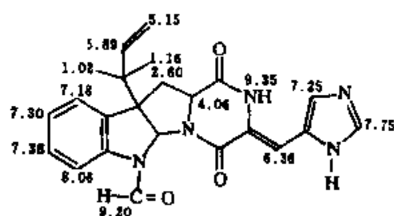
$759^{[435]}$



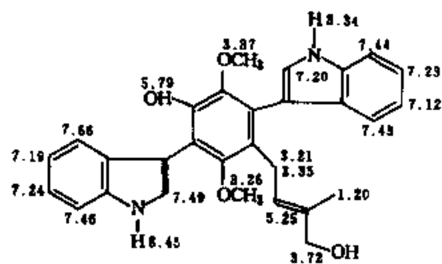
$760^{[435]}$



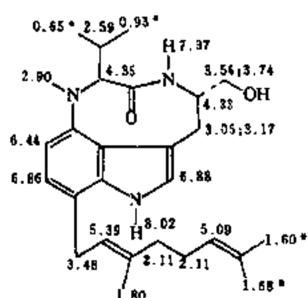
$761^{[436]}$



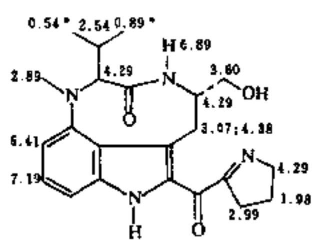
$762^{[437]}$



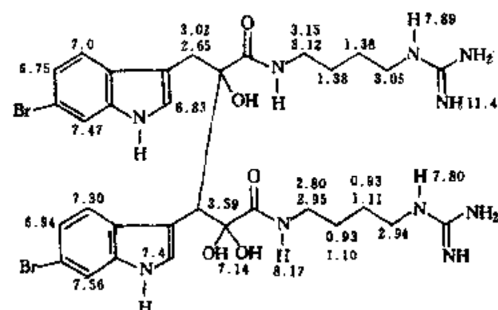
$763^{[438]}$



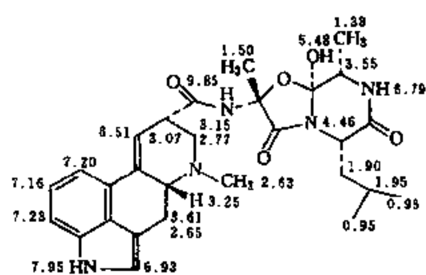
764[439]



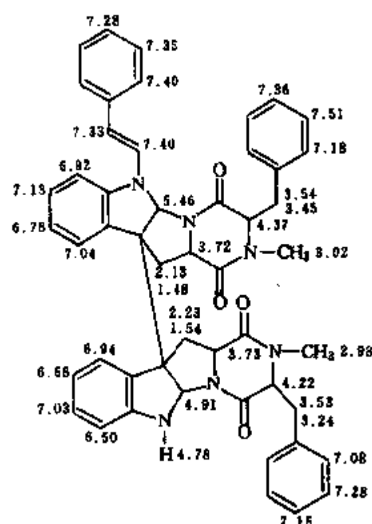
765[439]



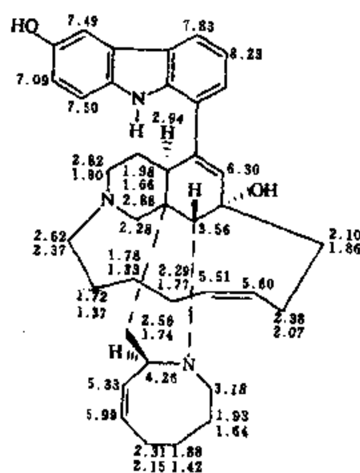
766[440]



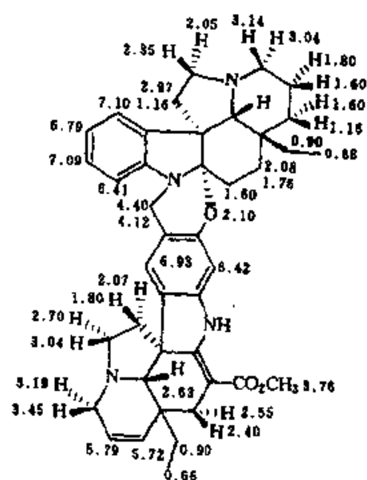
767[441]



768[442]



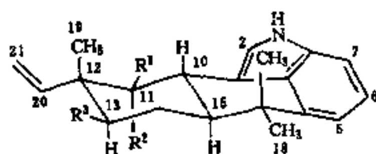
769[443]



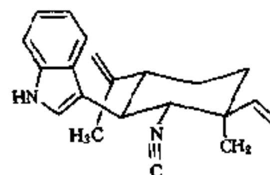
770[444]

表 6-4 吲哚生物碱 771～773 的^{1}H-NMR 化学位移和偶合常数[445]

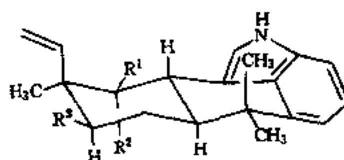
质子 \ 化合物	771	772	773
1-H	8.02 brs	8.05 brs	8.01 brs
2-H	7.59 dd(2,2)	6.93 dd(1.5,1.5)	7.02 d(2.5)
4-H	—	—	7.65 brd(8)
5-H	7.03 m	7.04 m	7.16 ddd(1,7,8)
6-H	7.18 m	7.20 m	7.08 ddd(1,7,8)
7-H	7.18 m	7.20 m	7.33 brd(8)
10-H	3.23 dd(11,11)	3.31 brd(12)	3.11 dd(11,11)
11-H	3.54 d(11)	4.40 d(3)	3.76 brd(11)
13ax-H	1.45 ddd(3,11,14)	4.30 dd(4,12)	1.65 to 1.84 4H
13eq-H	1.78 ddd(3,3,14)	—	
14ax-H	1.59 dddd(11,11,13,13)	1.99 ddd(12,12,12)	
14eq-H	1.85 dddd(3,3,3,13)	2.37 ddd(3,4,12)	
15-H	1.49 ddd(3,11,11)	2.09 ddd(3,12,12)	2.68 brdd(11,11)
17-H	1.15 s	1.14 s	1.53 s
18-H	1.46 s	1.52 s	4.53/4.47 brs
19-H	1.32 s	1.54 s	1.32 s
20-H	5.89 dd(11,17)	6.32 dd(11,18)	5.91 dd(11,17)
21*trans*-H	5.20 d(17)	5.37 d(18)	5.16 brd(17)
21*cis*-H	5.17 d(11)	5.42 d(11)	5.11 brd(11)



771. R^1 = —NC，R^2 = H，R^3 = H



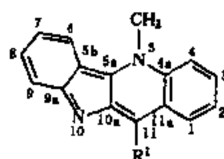
773



772. R^1 = H，R^2 = —NC，R^3 = Cl

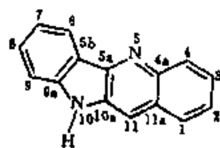
表 6-5 吲哚生物碱 774～777 的 ^{1}H-NMR 化学位移和偶合常数[446]

质子 \ 化合物	774	775	776	777
1-H	8.16 d(8.2)	8.47 d(8.1)	7.93 d(8.2)	7.96 d(8.1)
2-H	7.59 dd(8.2,7.3)	7.31 dd(8.1,6.6)	7.54 dd(8.2,6.7)	7.24 dd(8.1,6.6)
3-H	7.79 dd(8.9,7.3)	7.69 dd(8.3,6.6)	7.67 dd(8.5,6.7)	7.45 dd(7.7,6.6)
4-H	8.06 d(8.9)	7.72 d(8.3)	8.34 d(8.5)	7.92 d(7.7)
5-NCH_3	4.72 s	4.39 s		
5a-H				3.81s
6-H	8.13 d(8.5)	8.19d(8.4)	8.55 d(7.8)	8.95 d(8.0)
7-H	6.99 dd(8.5,6.6)	7.13 dd(8.4,7.3)	7.34 dd(7.8,7.3)	7.65 dd(8.0,6.7)
8-H	7.53 dd(8.6,6.6)	7.42 dd(8.3,7.3)	7.60 dd(8.1,7.3)	7.75 dd(8.5,6.7)
9-H	7.81 d(8.6)	7.50 d(8.3)	7.46 d(8.1)	7.72 d(8.5)
10-NH			8.20 br s	
10-NCH_3				4.27 s
11-H	8.73 s		8.04 s	8.75 s
11-OH		10.17 br s		
12-OH				9.87 br s

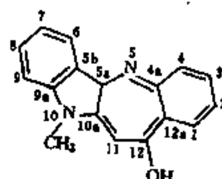


774. R^1 = H

775. R^1 = OH



776

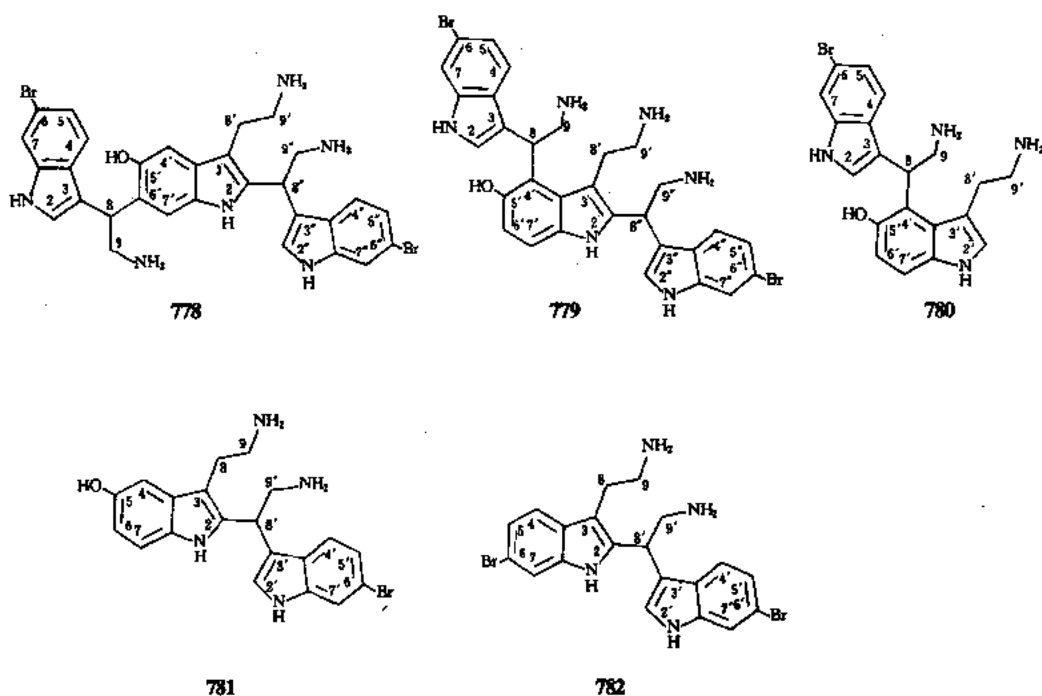


777

表 6-6 吲哚生物碱 778～782 的 ^{1}H-NMR 化学位移和偶合常数[447]

质子 \ 化合物	778	779	780
2-H	7.46 s	7.02 s	7.01 s
4-H	7.30 d(8.5)	7.64 d(8.5)	7.62 d(8.5)
5-H	7.04 dd(8.5,1.7)	7.19 dd(8.5,1.8)	7.18 dd(8.5,1.7)
6-H			
7-H	7.58 d(1.7)	7.56 d(1.8)	7.53 d(1.7)
8-H	5.18(7.8)	5.35 dd(10.0,5.2)	5.35 dd(5.2,10.0)
9-H	3.66 dd(7.8,12.6)	4.25 dd(12.1,10.0)	4.21 dd(12.3,10.0)
	3.68 dd(7.8,12.6)	3.78 dd(12.1,5.2)	3.72 dd(12.3,5.2)
2′-H			7.08 s
4′-H	7.15 s		
5′-H			
6′-H		6.91 d(8.6)	6.88 d(8.6)
7′-H	7.06 s	7.38 d(8.6)	7.28 d(8.6)
8′-H	3.25t(8)	3.58m	3.40m
		3.20m	3.17m
9′-H	3.04 dt(8,12)	2.88m	2.90m
	3.11 dt(8,12)	2.67m	2.76m
2″-H	7.31 s	7.37 s	
4″-H	7.53 d(8.5)	7.75 d(8.5)	
5″-H	7.13 dd(8.5,1.7)	7.16 dd(8.5,1.8)	
7″-H	7.56 d(1.7)	7.56d(1.8)	
8″-H	5.08 dd(7.1,9.1)	5.16 dd(8.2,6.8)	
9″-H	3.61 dd(12.8,7.1)	3.80 dd(12.7,6.8)	
	3.74 dd(12.8,9.1)	3.66 dd(12.7,8.2)	

质子 \ 化合物	781	782
4-H	6.94 d(1.7)	7.51 d(8.5)
5-H		7.20 dd(8.5,1.8)
6-H	6.74 dd(8.5,1.7)	
7-H	7.26 d(8.5)	7.60 d(1.8)
8-H	3.30m	3.27m
9-H	3.01m	3.07m
	2.94m	3.00m
2′-H	7.30 s	7.38 s
4′-H	7.52 d(8.5)	7.56 d(8.5)
5′-H	7.17 dd(8.5,1.7)	7.17 dd(8.5,1.8)
7′-H	7.57 d(1.7)	7.58 d(1.8)
8′-H	5.04 dd(8.5,6.8)	5.16 dd(8.6,6.9)
9′-H	3.80 dd(12.7,6.8)	3.84 dd(12.1,6.9)
	3.66 dd(12.7,8.5)	3.69 dd(12.1,8.6)

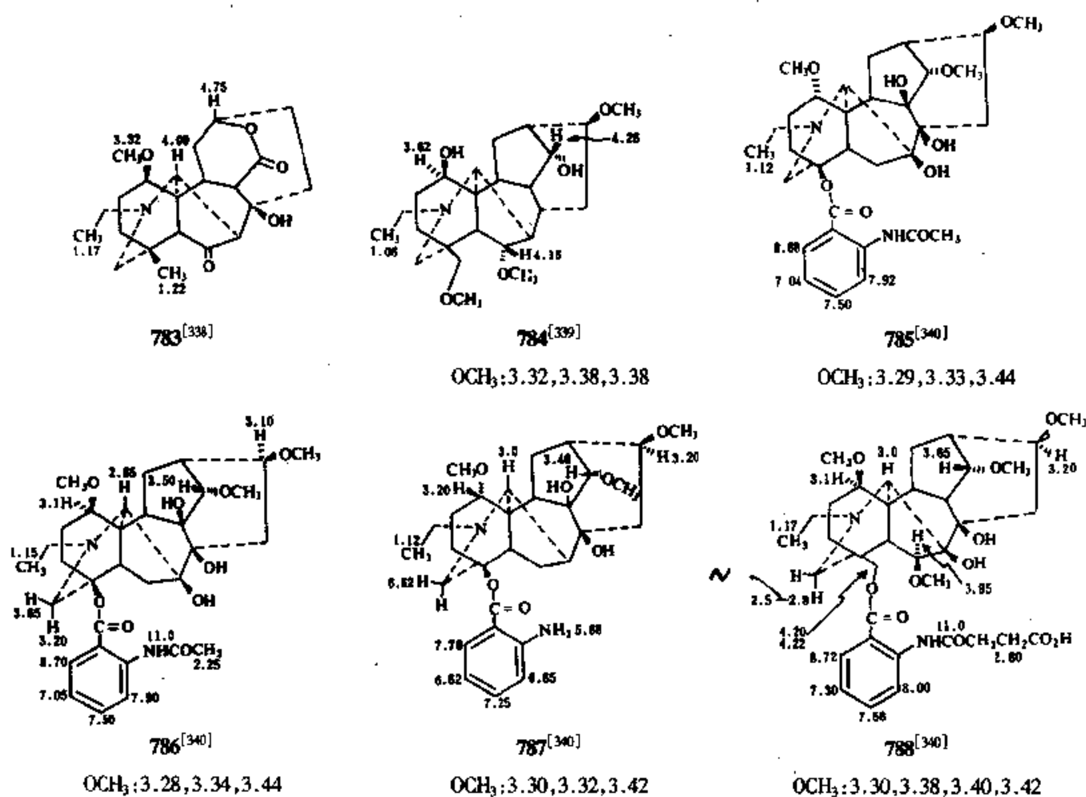


778　779　780

781　782

第六节　二萜生物碱类化合物的^{1}H-NMR 化学位移

一、乌头生物碱的^{1}H-NMR 化学位移



783[338]

784[339]
OCH$_3$:3.32,3.38,3.38

785[340]
OCH$_3$:3.29,3.33,3.44

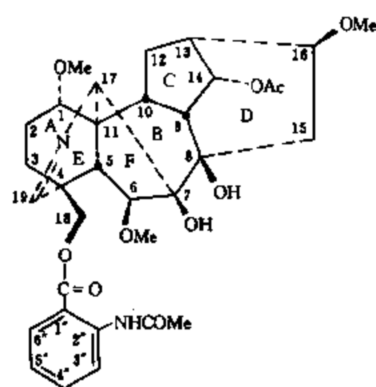
786[340]
OCH$_3$:3.28,3.34,3.44

787[340]
OCH$_3$:3.30,3.32,3.42

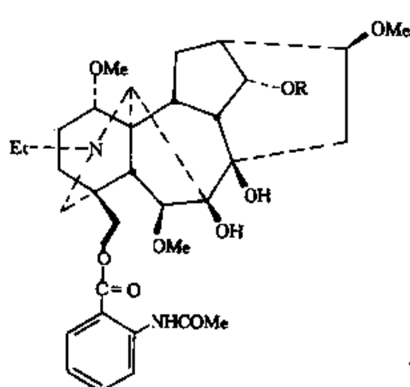
788[340]
OCH$_3$:3.30,3.38,3.40,3.42

表 6-7　C_{19}二萜生物碱 789~793 的^{1}H-NMR 化学位移和偶合常数[448]

质子＼化合物	789	790	791	792	793
1-H	3.32 m	3.05 m	3.01~2.97 m	3.63 brs	2.91 m
2-H	1.98~2.21 m	2.03~2.25 m	2.00~2.24 m	1.64~1.93 m	1.81~2.02 m
3-H	1.48~1.65 m	1.52~1.75 m	1.51~1.75 m	1.45~1.65 m	1.25~1.75 m
5-H	1.95 brs	1.83 brs	1.72 brs	1.84 brs	1.45 brs
6-H	3.80 brs	3.83 brs	3.86 s	3.99 s	3.51 s
9-H	3.08 m	3.10 m	3.03 m	2.95 m	3.33 m
10-H	2.11 m	1.85 m	2.07 m	1.93 m	1.94 m
12-H	1.65~2.55 m	1.82~2.83 m	1.75~2.85 m	1.90~2.03 m	1.90~2.13 m
13-H	2.50 m	2.95 m	2.29 m	2.30 m	2.51 m
14-H	4.83 t(4.5)	4.01 brs	3.56 t(4.6)	4.06 brs	4.68 t(4.8)
15-H	1.79~2.95 m	1.81~2.52 m	1.85~2.55 m	1.59~1.68 m	1.92~2.40 m
16-H	3.45 m	3.45 m	3.05 m	3.30 m	3.23 m
17-H	3.97 brs	3.25 m	2.91 brs	2.82 s	2.94 brs
18-H	4.40~4.57 d,d (9.7)	4.16 d(9.0)	4.13 brs	2.95~3.42 AB (9.3)	3.13 AB q (9.9)
19-H	7.55 brs	2.52~2.80 AB (10.5)	2.41~2.73 AB (11.9)	2.41 s	2.55 s
20-H	—	2.95 m	2.75~2.91 m	2.75~2.98 m	2.79~2.88 m
21-H	—	1.06 t(7.1)	1.03 t(7.2)	1.06 t(7.1)	1.02 t(7.1)
1-OMe	3.20 s	3.25 s	3.22 s	—	3.20 s
6-OMe	3.33 s	3.35 s	3.36 s	3.33 s	3.30 s
8-OMe	—	—	—	—	3.47 s
14-OMe	—	—	3.33 s	—	—
16-OMe	3.36 s	3.37 s	3.29 s	3.34 s	3.26 s
18-OMe	—	—	—	3.30 s	3.42 s
1-OH	—	—	—	7.30 brs	—
7-OH	2.62 brs	2.15 brs	2.05 brs	5.26 s	
8-OH	3.55 s	3.87 s	4.13 s	3.95 s	—
14-OH	—	2.77 brs	—	3.40 s	—
14-OAc	2.09 s	—	—	—	2.01 s
NH-Ac	10.93 s	10.98 s	10.97 s	—	—
	2.26 s	2.22 s	2.18 s	—	—
芳香氢					
3″-H	8.76 dd (7.3,1.5)	8.71 dd (7.2,1.4)	8.65 dd (8.5,1.3)	—	—
4″-H	7.61 ddd (7.7,7.0,1.4)	7.57 ddd (7.8,7.1,1.6)	7.52 ddd (7.6,7.0,1.5)	—	—
5″-H	7.15 ddd (8.0,7.5,1.3)	7.10 ddd (8.2,7.6,1.5)	7.09 ddd (8.0,7.5,1.5)	—	—
6″-H	7.98 dd (8.0,1.5)	7.98 dd (8.1,1.4)	7.92 dd (7.9,1.5)	—	—

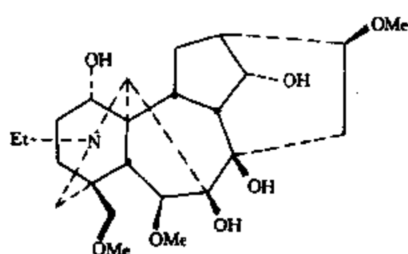


789

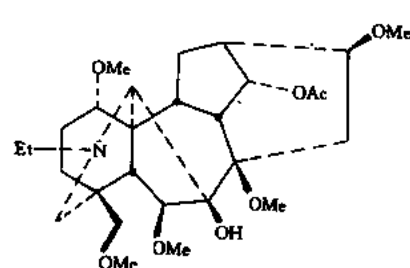


790. R = H

791. R = Me



792



793

二、六种基本骨架(Ⅰ～Ⅵ型)C_{19}二萜生物碱的^{1}H-NMR 化学位移[449]

表 6-8　C_{19}二萜生物碱 A 环的^{1}H-NMR 化学位移

结构类型 / 质子	Ⅰ 1α-OMe	Ⅰ 1α-OMe 15-脱氢	Ⅱ 1α-OMe	Ⅱ 3-OAc	Ⅲ 1α-OMe
1-H	3.14 ± 0.04	3.00 ± 0.02	3.10 ± 0.04	3.10 ± 0.04	3.01 ± 0.02
2-H_a	1.97 ± 0.09	2.16 ± 0.01	2.13 ± 0.11	2.37 ± 0.02	1.97 ± 0.03
2-H_b	2.34 ± 0.02	2.34 ± 0.02	2.36 ± 0.04	2.37 ± 0.02	2.28 ± 0.02
3-H_a	3.82 ± 0.05	3.65 ± 0.01	3.73 ± 0.05	4.90 ± 0.01	1.59 ± 0.09
3-H_b	—	—	—	—	1.62 ± 0.05

结构类型 / 质子	Ⅳ 1α-OMe	Ⅳ 1α-OH	Ⅳ 1β-OH	Ⅴ 1α-OMe	Ⅴ 1α-OH	Ⅵ 1α-OMe	Ⅵ 1α-OH
1-H	3.03 ± 0.00	3.67 ± 0.03	3.90	3.11 ± 0.04	3.72 ± 0.01	2.94 ± 0.01	3.66 ± 0.03
2-H_a	1.96 ± 0.01	1.54 ± 0.02	1.36	1.98 ± 0.00	1.67 ± 0.04	2.00 ± 0.10	1.52 ± 0.06
2-H_b	2.27 ± 0.03	1.88 ± 0.04	2.96	2.22 ± 0.00	1.85 ± 0.01	2.08 ± 0.08	1.75 ± 0.21
3-H_a	1.63 ± 0.00	1.54 ± 0.02	1.36	1.38 ± 0.01	1.67 ± 0.04	1.39 ± 0.12	1.63 ± 0.09
3-H_b	1.63 ± 0.00	1.54 ± 0.02	1.85	1.80 ± 0.00	1.67 ± 0.04	1.67 ± 0.16	1.75 ± 0.21

表 6-9 C_{19}二萜生物碱 B 环的^{1}H-NMR 化学位移

结构类型 / 质子	Ⅰ	Ⅱ	Ⅲ	Ⅳ	
	6α-OMe	6α-OMe	6α-OMe	6α-OH	6α-OMe
5-H	2.06±0.06	2.05±0.06	2.04±0.04	2.10±0.08	2.10±0.01
6-H_a	4.02±0.07	4.08±0.07	3.98±0.04	4.10±0.07	4.74±0.03
6-H_b	—	—	—	—	—
7-H	2.89±0.21	2.96±0.07	2.96±0.06	2.81±0.03	—
		(8-OAc)	(8-OAc)	(8-OAc)	
		1.97±0.11	2.08±0.01	2.01±0.01	1.93±0.00
		(8-OH)	(8-OH)	(8-OH)	(8-OH)

结构类型 / 质子	Ⅴ	Ⅵ			
	6-H	6-H	6β-OMe	6β-OH	6α-OH
5-H	1.76±0.11	1.79	1.78±0.09	1.59±0.11	2.13
6-H_a	1.56±0.06	1.60	3.92±0.07	4.41±0.09	4.45
6-H_b	1.90±0.04	2.30	—	—	—
7-H	2.10±0.02	—	—	—	—

表 6-10 C_{19}二萜生物碱 C 环的^{1}H-NMR 化学位移

结构类型 / 质子	Ⅰ		Ⅱ		Ⅲ	
	8-OAc 14-OAr	8-OH 14-OAr	8-OAc 14-OAr	8-OH 14-OAr	8-OAc 14-OAr	8-OH 14-OAr
9-H	2.90±0.01	2.52	2.91±0.02	2.54±0.02	2.90±0.01	2.54±0.00
10-H	2.01±0.11	2.13	2.10±0.07	2.10±0.07	2.06±0.03	2.06±0.03
12-H_a	2.01±0.11	2.13	2.10±0.07	2.10±0.07	2.06±0.03	2.06±0.03
12-H_b	2.66±0.30	2.58	2.72±0.20	2.54±0.10	2.78±0.02	2.59±0.00
13-H	—	—	—	—	—	—
14-H	4.89±0.09	5.00	4.87±0.02	5.14±0.02	4.87±0.02	5.15±0.00
		3.91		4.01		3.99
		(8,14-OH)		(8,14-OH)		(8,14-OH)

结构类型 / 质子	Ⅳ			Ⅴ		Ⅵ	
	8-OH 14-OAc	8-OH 14-OAr	8-OH 14-OH	8-OH 14-OH	8-OH 14-OAc	8-OH 14α-OMe	6-H 14α-OH
9-H	2.33±0.19	2.43±0.00	2.19±0.05	2.25±0.03	2.35	3.10±0.14	2.22
10-H	1.93±0.12	1.95±0.01	1.93±0.12	1.78±0.08	1.63	1.94±0.04	1.81
12-H_a	1.69±0.28	1.96±0.01	1.69±0.28	1.70±0.10	1.90	1.75±0.04	1.55
12-H_b	2.26±0.29	2.38±0.07	2.26±0.29	1.98±0.08	2.14	2.25±0.17	2.06
13-H	2.59±0.07	2.67±0.10	2.30±0.05	2.35±0.01	2.65	2.40±0.07	2.35
14-H	4.78±0.04	5.10±0.06	4.16±0.05	4.18±0.05	4.83	3.65±0.05	4.24

表 6-11　C_{19}二萜生物碱 D 环的^{1}H-NMR 化学位移

结构类型 \ 质子	Ⅰ	Ⅱ		Ⅲ	
	8-OAc 14-OAr	8-OAc 14-OAr	8-OH 14-OAr	8-OAc 14-OAr	8-OH 14-OAr
15-H_a	4.51±0.06	2.45±0.05	2.28±0.06	2.45±0.03	2.29±0.03
15-H_b	—	3.06±0.08	2.57±0.04	3.05±0.03	2.55±0.03
15-OH	4.40±0.09	—	—	—	—
16-H	3.29±0.10 3.88(16α-OMe)	3.34±0.05	—	3.37±0.05	—

结构类型 \ 质子	Ⅳ	Ⅴ		Ⅵ
	8-OH 14-OAc	8-OH 14-OH	8-OH 14-OAc	8-OH 14α-OMe
15-H_a	2.09±0.16	2.07±0.01	1.90	1.69±0.09
15-H_b	2.37±0.13	2.43±0.01	2.42	2.80±0.20
15-OH	—	—	—	—
16-H	3.20±0.17	3.39±0.02	3.20	3.29±0.10

表 6-12　C_{19}二萜生物碱 E 环的^{1}H-NMR 化学位移

结构类型 \ 质子	Ⅰ	Ⅱ	Ⅲ	Ⅳ	
	1α-OMe	1α-OMe	1α-OMe	8-OAc	8-OH
17-H	3.02±0.22	2.96±0.11	3.02±0.12	2.94±0.05	2.60±0.07
19-H_a	2.44±0.13	2.35±0.09	2.37±0.11	2.15±0.21	2.15±0.21
19-H_b	2.89±0.04	2.85±0.09	2.99±0.10	2.70±0.16	2.70±0.16

结构类型 \ 质子	Ⅴ			Ⅵ	
	1-脱氢	1α-OH	1α-OMe	1α-OH	1α-OMe
17-H	3.34±0.00	2.80±0.01	3.10±0.07	2.95±0.20	2.89±0.01
19-H_a	2.15±0.21	2.07±0.01	2.02±0.01	2.44±0.09	2.40±0.14
19-H_b	2.70±0.16	2.34±0.00	2.53±0.02	2.61±0.18	2.62±0.02

表 6-13　C_{19}二萜生物碱 *N*-乙基的^{1}H-NMR 化学位移(一)

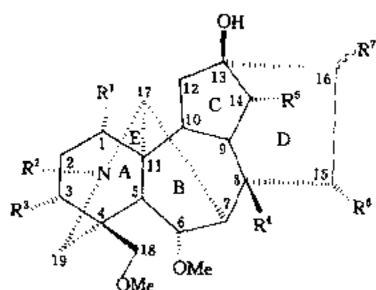
结构类型 \ 质子	Ⅰ		Ⅱ			Ⅲ	
	3α-OH	3α-OAc	3α-OH	3α-OAc	8-OH	8-OAc	8-OH
18-H_a	3.56±0.12	2.96	3.49±0.01	2.98±0.02	3.74±0.03	3.14±0.02	3.31±0.01
18-H_b	3.61±0.08	3.83	3.63±0.01	3.93±0.09	—	3.60±0.01	3.68±0.02

结构类型 \ 质子	Ⅳ	Ⅴ		Ⅵ	
	8-OH	18-OH	18-OMe	18-OH	18-OMe
18-H_a	3.20±0.16	3.27	3.00±0.01	3.35±0.01	3.19±0.15
18-H_b	3.59±0.14	3.41	3.13±0.02	3.64±0.01	3.28±0.06

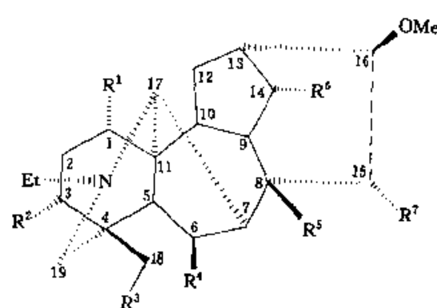
表 6-14　C_{19}二萜生物碱 *N*-乙基的^{1}H-NMR 化学位移(二)

结构类型 \ 质子	Ⅰ	Ⅱ	Ⅲ	Ⅳ		Ⅴ	Ⅵ
	15-OH	15-H	15-H	15-H	15-OH	15-H	15-H
20-H_a	2.46±0.09	2.54±0.04	2.53±0.06	2.50±0.05	2.36±0.05	2.49±0.03	2.89±0.05
20-H_b	2.69±0.07	—	—	—	2.69±0.09	—	—
21-H_3	1.09±0.01	1.10±0.01	1.07±0.01	1.08±0.05	1.08±0.05	1.09±0.03	1.07±0.03

C_{19}-二萜生物碱的结构类型及其所含主要生物碱



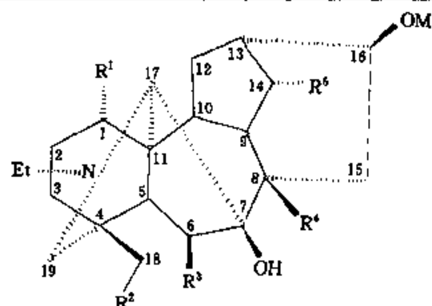
结构式 **794～825**



结构式 **826～839**

类型	R^1	R^2	R^3	R^4	R^5	R^6	R^7
Ⅰ.乌头碱型							
794	OMe	Et	OH	OAc	OBz	OH	β-OMe
795	OMe	Et	OH	OH	OBz	OH	β-OMe
796	OMe	Et	OH	OH	OH	OH	β-OMe
797	OMe	Et	OH	OMe	OH	OH	β-OMe
798	OMe	Et	OH	OEt	OBz	OH	β-OMe
799	OMe	Et	OAc	OEt	OBz	OH	β-OMe
800	OMe	Me	OH	OAc	OBz	OH	β-OMe
801	OMe	Me	OH	OMe	OBz	OH	β-OMe
802	OMe	Me	H	OAc	OBz	OH	β-OMe
803	OH	Me	H	OAc	OBz	OH	β-OMe
804	OMe	Et	H	OAc	OBz	OH	β-OMe
805	OMe	Et	OH	H	OH	=O	β-OMe
806	OMe	Et	OH	H	OH	=O	α-OMe
Ⅱ.假乌头碱型							
807	OMe	Et	OH	OAc	OVr	H	β-OMe
808	OMe	Et	OH	OH	OVr	H	β-OMe
809	OMe	Et	OH	OH	OH	H	β-OMe
810	OMe	Et	OH	Olip	OVr	H	β-OMe
811	OMe	Et	OH	OAc	OAs	H	β-OMe
812	OMe	Et	OH	Olip	OAs	H	β-OMe
813	OMe	Et	OH	OH	OAs	H	β-OMe
814	OMe	Et	OH	OAc	OBz	H	β-OMe
815	OMe	Et	OH	Olip	OBz	H	β-OMe
816	OMe	Et	OH	OH	OBz	H	β-OMe
817	OMe	Et	OAc	OAc	OVr	H	β-OMe
818	OMe	Et	OAc	OAc	OAs	H	β-OMe
819	OMe	Et	OAc	OH	OVr	H	β-OMe
Ⅲ.白乌头碱型							
820	OMe	Et	H	OAc	OVr	H	β-OMe
821	OMe	Et	H	OH	OVr	H	β-OMe
822	OMe	Et	H	OLip	OVr	H	β-OMe
823	OMe	Et	H	OH	OH	H	β-OMe
824	OMe	Et	H	OAc	OBz	H	β-OMe
825	OMe	Et	H	OAc	OAs	H	β-OMe

类型	R^1	R^2	R^3	R^4	R^5	R^6	R^7
Ⅳ.尼奥灵型							
826	α-OH	H	OMe	OMe	OH	OH	H
827	α-OH	H	OMe	OH	OH	OH	H
828	α-OH	H	OMe	OH	OH	OAc	H
829	α-OAc	H	OMe	OAc	OH	OAc	H
830	=O	H	OMe	=O	OH	OAc	H
831	α-OMe	H	OMe	OMe	OAc	OVr	H
832	α-OMe	OH	OMe	OMe	OH	OVr	H
833	α-OH	H	OMe	OMe	OAc	OH	OH
834	β-OH	H	OMe	OMe	OH	OH	OH
835	α-OAc	H	OMe	OMe	OH	OAc	H
Ⅴ.异塔拉定型							
836	OH	H	OMe	H	OH	OH	H
837	OH	H	OH	H	OH	OH	H
838	OMe	H	OMe	H	OH	OH	H
839	OMe	H	OMe	H	OH	OAc	H



结构式 **840～845**

类型	R^1	R^2	R^3	R^4	R^5
Ⅵ.牛扁碱型					
840	OH	OH	β-OMe	OH	OMe
841	OMe	OH	β-OMe	OH	OMe
842	OH	OMe	β-OH	OH	OMe
843	OMe	OMe	β-OH	OH	OMe
844	OH	OMe	H	OH	OH
845	OH	OMe	α-OH	OMe	OAc

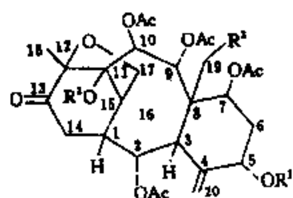
表 6-15 C_{20}二萜生物碱 ^{1}H-NMR 峰多重性和偶合常数与平面夹角的关系

质子	平面夹角 椅式	平面夹角 船式	构型	峰多重性	预算值 J/Hz	实测值 J/Hz
1-H_{α}/2-H_{α}	70°	55°				
1-H_{α}/2-H_{β}	50°	60°			6.0	
1-H_{β}/2-H_{α}	180°	180°	1β-H	t	6.5	6.0~8.8
				dd		5.8~7.5
1-H_{β}/2-H_{β}	50°	55°			7.6	7.5~11.0
				m	–	—
2-H_{α}/3-H_{α}	70°	50°				
2-H_{α}/3-H_{β}	50°	65°	3β-H	t	5.0	8.2
				dd		4.0~6.0
2-H_{β}/3-H_{α}	165°	180°			9.0	8.0~13.0
				m	—	—
2-H_{β}/3-H_{β}	50°	65°			5.0	
5-H/6-H_{α}	25°		5β-H	d	6.0	4.2~7.0
				m	—	—
5-H/6-H_{β}	95°				0.4	
6-H_{α}/7-H	110°				1.0	
6-H_{β}/7-H	10°		6β-H	d	7.4	6.0~8.0
				dd		5.0, 11.0
				m	—	—
9-H/10-H_{α}	20°				6.5	6.5~6.6
				m		—
9-H/14-H_{α}	30°		9β-H	t	5.6	6.0
				dd		4.7~5.1
10-H/12-H_{α}	0°					
10-H/12-H_{β}	120°				4.4	
12-H_{α}/13-H	80°				6.0	
12-H_{β}/13-H	40°					
14-H_{α}/13-H	75°		14β-H	d	1.8	4.0~6.0
				m		—
13-H/16-H_{α}	130°				6.0	
15-H_{α}/8-H	40°				2.5	4.0~16.0
15-H_{β}/8-H	80°					
15-H_{α}/16-H_{α}	170°		15β-H	t	9.6	4.0
				d		2.0~6.1
				dd		2.0~7.0
				m	—	
15-H_{α}/16-H_{β}	50°		15α-OH	d	1.3	2.0~4.0
			16α-H	d		4.0~8.0
				dd		4.5~7.0
						8.0~10.0
				m	—	—
17-H_{α}/7-H_{α}	90°		17α-H	br s	1.0	
18-H_{a}/18-H_{b}	120°		18-H	d s	4.4	8.0~20.0
19-H_{a}/19-H_{b}	120°		19-H	d	4.4	10.0~12.0
						6.0~9.0
				dd		16.0
20-H_{a}/20-H_{b}	120°		20-H	t	4.4	7.2
				dd		4.0~8.0
						7.0~14.0
				m	—	
			21-H	t		6.0~8.0

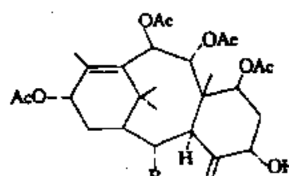
三、紫杉烷类二萜生物碱的^{1}H-NMR化学位移和偶合常数[450]

表 6-16　紫杉烷生物碱 846～849 的^{1}H-NMR化学位移和偶合常数

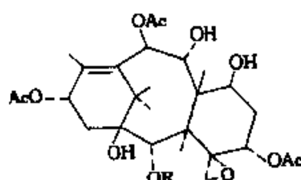
质子＼化合物	846	847	848	849
1-H	2.42 dd(2.5,11.9)	1.79 m		
2-H	6.16 dd(2.5,10.5)	1.74 ddd(1.5,5.3,15.7)	4.00 d(3.5)	6.17 d(7.0)
2′-H		1.90 m		
3-H	3.64 d(10.5)	3.22 br d(4.8)	3.12 d(3.5)	4.52 d(7.0)
5-H	4.40 m	4.30 br t(3.0)	4.26 t(3.0)	5.29 dd(1.7,9.8)
6-H	1.63 ddd(3.9,10.6,14.3)	1.66 ddd(3.5,11.4,13.8)	1.92 ddd(2.8,4.4,14.8)	2.37 ddd(2.1,10.9,14.7)
6′-H	2.17 ddd(2.4,6.3,14.3)	1.97 ddd(2.5,5.1,13.8)	2.07 m	3.10 ddd(6.7,9.7,14.7)
7-H	5.44 dd(6.3,10.7)	5.69 dd(5.1,11.4)	4.26 dd(4.4,11.5)	4.83 dd(6.7,10.7)
9-H	5.29 d(3.1)	5.82 d(11.0)	4.49 d(10.5)	
10-H	5.48 d(3.1)	6.27 d(11.0)	5.99 d(10.5)	6.10s
13-H		5.74 ddd(1.3,4.7,10.6)	6.04 dd(6.3,9.7)	5.26 br d(8.0)
14-H	3.00 dd(12.0,19.1)	1.09 dd(4.8,15.3)	1.84 dd(6.3,15.0)	2.79 dd(9.4,15.3)
14′-H	2.71 d(19.1)	2.79 ddd(9.0,10.6,15.3)	2.56 dd(9.7,15.0)	2.89 dd(7.0,15.3)
16-Me	1.59 s	1.61 s	1.46 s	1.58 s
17-H	3.70 d(8.0)			
17′-H	4.19 d(8.0)			
17-Me		1.00 s	1.23 s	1.41 s
18-Me	1.17 s	2.20 d(1.3)	2.12 d(1.5)	2.48 s
19-H	4.29 d(12.1)			
19′-H	4.41 d(12.1)			
19-Me		0.81 s	1.45 s	2.21 s
20-H	4.46 s	4.84 d(1.4)	2.44 d(4.7)	4.49 d(8.2)
20′-H	5.32 s	5.18 brs	3.71 d(4.7)	4.56 d(8.2)
OAc	1.96 s	1.98 s	2.08 s	2.40 s
	1.99 s	2.03 s	2.13 s	
	2.10 s×2	2.05 s	2.17 s	
	2.18 s	2.06 s		
OBz				7.42 t
				7.50 t
				8.32 d
1″-H				4.67 d(7.5)
2″-H				3.70 dd(7.5,8.7)
3″-H				3.89 t(8.7)
4″-H				3.96 m
5″-H				4.14 dd(5.1,11.3)
5″-H				3.50 dd(10.1,11.3)



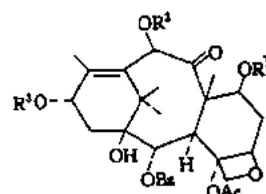
846. R^1 = H, R^2 = OH, R^3 = Ac



847. R = H



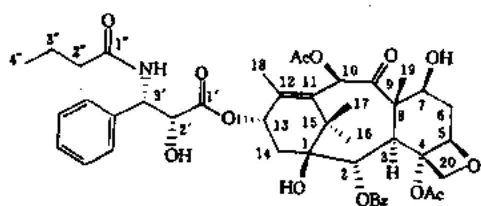
848. R = H



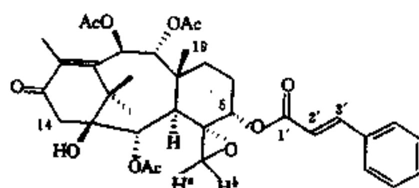
849. R^1 = β-木糖, R^2 = H, R^3 = H

表 6-17　紫杉烷生物碱 850～854 的¹H-NMR 化学位移和偶合常数[451]

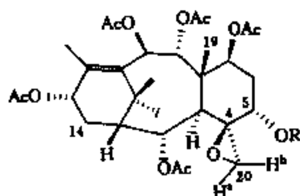
质子＼化合物	850	851	852	853	854
1-H	—	1.72 d(8.4)	—	5.62 d(3.9)	5.64 d(5.5)
2-H	5.68 d(7.0)	5.54 d(3.7)	—	3.49 d(3.9)	2.69 d(5.5)
3-H	3.79 d(7.0)	2.86 d(3.7)	2.57 brs	4.35 brs	4.80 dd (8.1,2.6)
5-H	4.94 brd(9.2)	4.21 t(3.1)	4.14 t(3.0)	—	2.35 m
6α-H	2.54 m	1.14 m	1.71 m		1.90 m
6β-H	1.86 m	1.96 m	1.41 m	—	5.25 t(9.2)
7-H	4.40 ddd (11.0,6.3,4.0)	5.40 dd (12.0,4.3)	4.19 dd (11.0,5.0)	5.95 d(10.2)	5.84 d(11.0)
9-H	—	5.97 d(11.2)	3.61 d(10.2)	6.09 d(10.2)	6.05 d(11.0)
10-H	6.29 s	6.24 d(11.2)	4.03 d(10.2)	—	5.72 br dd (9.7,3.3)
13-H	6.24 brt(9.0)	5.83 br t(8.3)	3.88 t(8.7)	3.22 d(19.4)	2.40 dd (15.5,9.7)
14α-H	2.30 m	1.29 dd (15.0,7.0)	0.99 dd (14.7,8.8)	2.74 d(19.4)	2.25 dd (15.5,3.7)
14β-H	2.30 m	2.71 dt (15.0,8.7)	2.19 dt (14.7,8.5)	1.65 s	1.65 s
16-H	1.17 s	1.69 s	1.39 s	1.24 s	1.08 s
17-H	1.26 s	1.09 s	0.78 s	2.31 brs	2.03 brs
18-H	1.82 br s	2.24 d(1.3)	1.62 s	1.03 s	1.45 s
19-H	1.66 s	1.20 s	0.82 s	2.90 d(4.4)	4.41 d(7.7)
20a(α)-H	4.28 d(8.6)	3.47 d(5.3)	5.04 s	2.57 d(4.4)	4.36 d(7.7)
20b(β)-H	4.20 d(8.6)	2.30 d(5.3)	4.74 s	2.14 s,2.11 s, 2.07 s	2.12 s,2.10 s, 2.10 s,2.08 s 2.01 s
Ac	2.35 s,2.26 s	2.09 s,2.04 s, 2.03 s,1.97 s, 1.94 s	—		

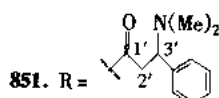


850

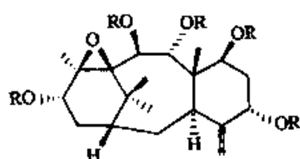


853

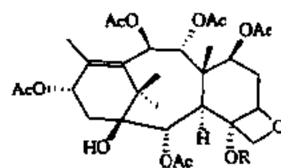




851. R =



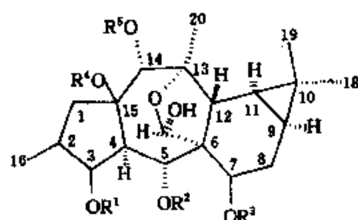
852. R = H



854. R = H

表 6-18　紫杉烷生物碱 855～858 的 ^{1}H-NMR 化学位移和偶合常数[452]

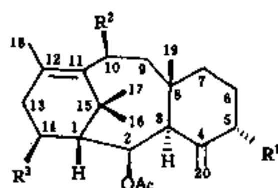
质子 \ 化合物	855	856	857	858
1β-H	3.05 dd(8.4,14.7)	3.08 dd(8.4,15.1)	3.28 dd(8.4,15.1)	2.41 dd(8.4,15.0)
1α-H	1.60 dd(3.1,14.7)	1.57 m	1.60 m	1.69 m
2-H	1.90 m	1.91 m	1.93 m	2.01 m
3-H	4.99 t(3.1)	4.92 t(3.1)	4.96 t(3.0)	5.06 t(3.6)
4-H	2.64 dd(3.1,10.7)	2.60 dd(3.1,10.8)	2.64 dd(3.0,10.7)	3.19 dd(3.4,10.7)
5-H	5.78 d(10.7)	5.80 d(10.8)	5.87 d(10.7)	5.85 d(10.7)
7-H	5.14 dd(2.2,11.5)	4.98 dd(2.5,11.0)	5.19 dd(2.5,10.0)	5.14 dd(2.5,11.6)
8β-H	1.92 m	1.80 m	1.81 m	1.82 m
8α-H	1.34 m	1.11 m	1.23 m	1.26 m
9-H	0.91 m	0.97 brd(7.0)	0.98 brd(7.1)	0.96 m
11-H	0.86 m	0.87 brd(7.5)	0.87 brd(7.5)	0.90 m
12-H	2.44 d(7.0)	2.45 d(7.5)	2.50 d(7.5)	2.46 d(6.8)
14-H	4.15 s	4.18 s	4.20 s	5.60 s
16-H	0.79 d(6.7)	0.79 d(6.6)	0.80 d(6.6)	0.77 d(6.6)
17-H	5.55 s	5.58 s	5.66 s	5.68 s
18-H	1.04 s	1.03 s	1.08 s	1.05 s
19-H	0.97 s	0.99 s	1.05 s	1.01 s
20-H	1.51 s	1.25 s	1.31 s	1.33 s
R^1-H	2.04 s	2.04 s	2.07 s	2.06 s
R^2-H	1.79 s	2.02 s	2.05 s	1.84 s
R^3-H	6.76 q(6.8)	6.62 q(7.8)	6.74 q(6.0)	6.82 q(6.4)
	1.79 brs	1.71 brs	1.73 brs	1.91 brs
	1.77 d(6.8)	1.56 d(7.8)	1.58 d(6.0)	1.79 d(6.4)
R^4-H	2.03 s	6.40 q(7.6)	7.85 brd(7.7)	7.00 q(7.4)
		1.73 brs	7.49 d(7.7)	1.91 brs
		1.61 d(7.6)	7.37 t(7.7)	1.82 d(7.4)
R^5-H				2.05 s

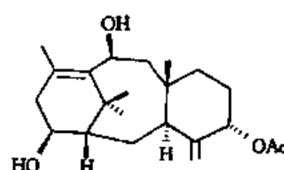


855. $R^1 = R^2 = R^4$ = —$COCH_3$, R^3 = —巴豆酰, R^5 = —H
856. $R^1 = R^2$ = —$COCH_3$, $R^3 = R^4$ = —巴豆酰, R^5 = —H
857. $R^1 = R^2$ = —$COCH_3$, R^3 = —巴豆酰, R^4 = —COC_6H_5, R^5 = H
858. $R^1 = R^2 = R^5$ = —$COCH_3$, $R^3 = R^4$ = —巴豆酰

表 6-19　紫杉烷生物碱 859～862 的^{1}H-NMR 化学位移和偶合常数[453]

质子＼化合物	859	860	861	862
1-H	1.69 br d(1.9)	1.78 d(2.1)	1.77 d(2.2)	1.65 m
2-H/2-H$_2$	5.36 dd(6.2,2.0)	5.32 dd(6.3,2.2)	5.33 dd(6.3,2.2)	1.73 m/1.66 m
3-H	2.82 d(6.1)	3.19 d(6.2)	3.19 d(6.3)	2.57 d(5.1)
5-H	5.19 t(2.7)	4.14 t(2.8)	4.14 t(2.9)	5.27 d(2.8)
6a-H	1.72 m	1.66 m	1.65 m	1.73 m
6b-H	1.72 m	1.66 m	1.65 m	1.73 m
7α-H	1.15 m	1.05 m	1.06 m	1.16 m
7β-H	1.86 m	2.04 m	2.03 m	1.88 m
9α-H	1.61 dd(14.9,5.6)	1.61 dd(14.8,5.6)	1.61 dd(14.8,5.6)	1.58 dd(14.5,5.5)
9β-H	2.29 dd(14.8,11.8)	2.26 dd(14.7,11.7)	2.27 dd(14.8,11.7)	2.24 dd(14.4,11.9)
10-H	5.05 dd(11.8,5.6)	5.12 dd(11.7,5.6)	5.12 dd(11.7,5.6)	5.11 dd(11.8,5.6)
13α-H	2.56 dd(18.5,8.8)	2.74 dd(18.8,9.3)	2.75 dd(18.9,9.3)	2.47 d(7.1)
13β-H	2.46 dd(18.6,5.3)	2.29 dd(18.4,4.3)	2.27 dd(18.3,4.2)	2.47 t(7.1)
14-H	4.04 dd(8.5,5.5)	4.99 dd(9.3,4.7)	4.98 dd(9.3,4.7)	3.71 t(7.1)
16-Me	1.18 s	1.13 s	1.14 s	1.18 s
17-Me	1.66 s	1.68 s	1.69 s	1.54 s
18-Me	1.94 s	1.95 s	1.95 s	1.92 s
19-Me	0.78 s	0.78 s	0.78 s	0.66 s
20a-H	5.21 brs	5.06 brs	5.07 brs	5.10 brs
20b-H	4.84 brs	4.73 t(1.4)	4.72 t(1.5)	4.77 brd(1.2)
2′-H$_2$/2′-H		2.26 q(7.6)	2.47 七重峰(7.0)	
3′a-H				
3′b-H				
3′-Me		1.08 t(7.6)	1.11 d(7.0)	
4′-Me			1.09 d(7.0)	
2-OAc-CH$_3$	2.03 s	2.00 s	2.00 s	
5-OAc-CH$_3$	2.09 s			2.05 s



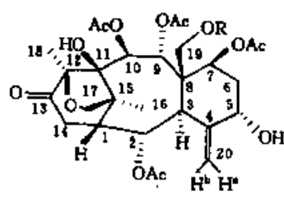


862

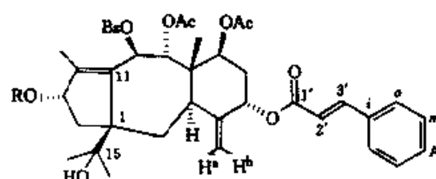
	R^1	R^2	R^3
859.	OAc	OH	OH
860.	OH	OH	OCOCH$_2$CH$_3$ (1′ 2′ 3′)
861.	OH	OH	OCOCH(CH$_3$)$_2$ (1′ 2′ 3′ 4′)

表 6-20 紫杉烷生物碱 863～865 的 ^{1}H-NMR 化学位移和偶合常数[454]

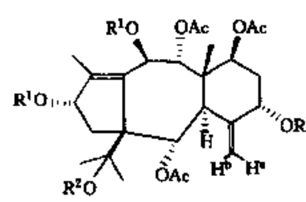
质子＼化合物	863	864	865
1-H	2.42 brd(1.5)	—	—
2α-H	—	1.47 brd(14.3)	—
2β-H	6.16 dd(10.2,2.0)	2.40 dd(14.3,9.1)	5.97 d(9.4)
3-H	3.63 d(10.2)	2.86 d(9.1)	3.18 d(9.4)
5-H	4.38 brt(2.5)	5.52 dd(3.9,2.1)	5.26 br t(2.5)
6α-H	2.16 m	2.04 m	1.98 m
6β-H	1.62 m	1.94 m	1.80 m
7-H	5.44 dd(10.5,6.1)	5.66 dd(11.3,5.6)	5.37 dd(10.8,5.0)
9-H	5.48 d(3.1)	6.04 brd(10.6)	5.74 brd(10.8)
10-H	5.28 d(3.1)	6.67 d(10.6)	6.31 d(10.8)
13-H	—	4.49 brt(7.2)	5.60 brt(7.7)
14α-H	2.70 d(19.2)	1.21 dd(13.9,7.1)	1.93 dd(14.9,8.0)
14β-H	3.00 dd(19.2,11.5)	2.37 dd(13.9,7.5)	2.46 dd(14.9,7.0)
16-H	1.59 s	1.31 s	1.70 s
17-H	4.19 d(8.0) 3.69 d(8.0)	1.00 s	1.55 s
18-H	1.17 s	2.15 s	2.01 s
19-H	4.40 d(12.3) 4.28 d(12.3)	0.92 s	0.99 s
20a-H	5.31 s	5.31 s	4.61 s
20b-H	4.44 s	4.92 s	5.28 s
Ac	2.18 s,2.11 s,2.10 s, 1.99 s,1.96 s	2.06 s,1.75 s	2.12 s,2.07 s,2.06 s, 2.05 s,2.01 s,1.86 s



863. R = Ac



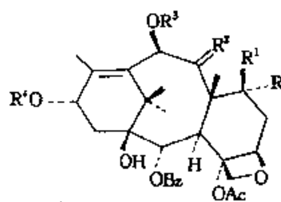
864. R = H



865. R^1 = Ac
R^2 = $CONHCOCCl_3$

表 6-21 紫杉烷生物碱 866,867 的 ^{1}H-NMR 化学位移和偶合常数[455]

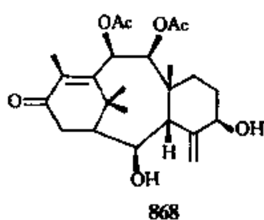
质子＼化合物	866	867	质子＼化合物	866	867
2-H	5.64 d(7.0)	5.75 d(5.8)	OAc	2.27 s,2.23 s	2.23 s,2.10 s
3-H	3.76 d(7.0)	3.10 d(5.8)	OBz		
5-H	4.94 dd(2.0,9.6)	4.90 d(8.9)	2″,6″-H	8.05 d(7.2)	8.07 d(7.5)
6a-H	2.54 ddd(6.7,9.6,14.8)	2.49 dd(8.5,15.0)	3″,5″-H	7.51 t(7.7)	7.47 t(7.7)
6b-H	1.87 ddd(2.0,10.8,14.8)	1.92 dd(9.3,15.0)	4″-H	7.62 t(7.4)	7.60 t(7.4)
7-H	4.39 dd(6.7,10.8)	4.33 t(8.5)	2′-H	4.49 d(5.1)	4.75 d(2.1)
9-H		4.39 d(10.7)	3′-H	5.03 d(5.1)	5.82 dd(2.1,9.0)
10-H	6.25 s	6.12 d(10.7)	3′-NH		7.37 d(9.0)
13-H	6.09 brt(8.7)	6.09 brt(8.5)	Ph		
14a-H	2.30 dd(9.1,15.3)	2.34 dd(8.5,15.0)	2″,6″-H	7.40 m	7.48 d(7.4)
14b-H	2.31 dd(8.5,15.3)	2.10 dd(7.8,15.0)	3″,5″-H	7.40 m	7.36 t(7.5)
16-CH_3	1.12 s	1.63 s	4″-H	7.35 m	7.30 t(7.3)
17-CH_3	1.21 s	1.20 s	NBz		
18-CH_3	1.66 s	1.72 d(1.0)	2″,6″-H		7.78 d(7.4)
19-CH_3	1.66 s	1.80 s	3″,5″-H		7.42 d(7.6)
20a-H	4.28 d(8.5)	4.28 d(8.3)	4″-H		7.49 t(7.8)
20b-H	4.15 d(8.5)	4.19 d(8.3)			



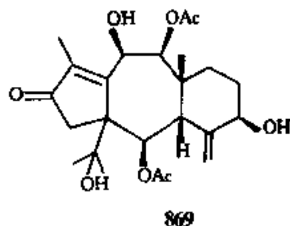
	R	R¹	R²	R³	R⁴
866.	H	OH	—O—	Ac	1′ 2′ 3′ COCHOHCHOHPh
867.	H	OH	H / OH	Ac	1′ 2′ 3′ COCHOHCH(Ph)NHBz

表 6-22　紫杉烷生物碱 868～870 的 ^{1}H-NMR 化学位移和偶合常数[456]

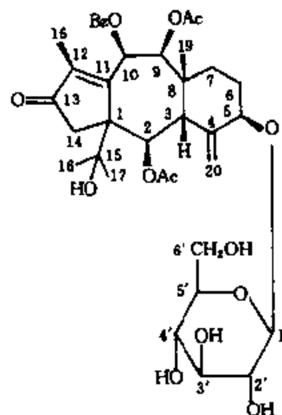
质子＼化合物	868	869	870	质子＼化合物	868	869	870
1-H	2.34 dd (7.0,2.4)			17-Me	1.16	1.05	1.23
2β-H	4.32 dd (6.5,2.4)	5.67 brs	6.14 d(9.5)	18-Me	2.21	2.03	1.88
3α-H	3.48 d(6.5)	3.17 brs	2.98 d(9.5)	19-Me	0.92	1.32	1.02
5β-H	4.32 t(2.8)	4.23 brs	4.34 brs	20-H	5.25 s,5.57 s	4.39 s,5.09 s	4.66 s,5.21 s
6-H	1.64,1.76 m	NA	1.77,1.93 m	OAc	2.04 s,2.07 s	1.93 s,2.13 s	1.78 s,2.06 s
7-H	1.64,1.83 m	NA	1.65,1.82 m	*p*-Ph			7.56 t(7.0)
9β-H	5.79 d(10.5)	5.94 d(9.0)	6.09 d(10.8)	*o*-Ph			7.88 d(7.5)
10α-H	6.09 d(10.5)	4.69 brd(9.0)	6.58 d(10.8)	*m*-Ph			7.43 t(7.5)
14α-H	2.26 d(19.8)	2.28 d(18.5)	2.48 d(18.5)	1′-H			4.15 d(7.5)
14β-H	2.80 dd (19.8,7.0)	2.63 d(18.5)	2.76 d(18.5)	2′-H			3.33 brt(7.5)
16-Me	1.69	1.05	1.22	3′-H			3.45 brt(7.5)
				4′-H			3.62 brt(7.5)
				5′-H			3.24 m
				6′-H			3.88 brs



868



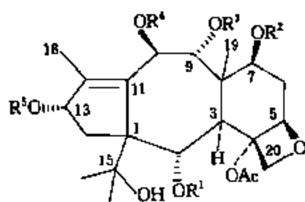
869



870

表 6-23 紫杉烷生物碱 871～875 的^{1}H-NMR 化学位移和偶合常数

质子 \ 化合物	871	872	873	874	875
2-H	6.14 d(7.3)	5.85 d(7.4)	6.46 d(7.8)	6.55 d(7.2)	6.12 d(7.8)
3-H	3.23 d(7.3)	3.10 d(7.4)	3.12 d(7.8)	3.19 d(7.2)	3.16 d(7.8)
5-H	4.93 d(7.5)	4.96 d(7.5)	4.97 d(7.6)	4.97 d(7.5)	4.94 d(7.4)
6-H	2.72 m	2.73 dd(15.3;7.8)	2.56 m	2.72 m	2.54 m
6'-H	2.00 m	2.02 m	1.90 dd(15.0;8.7)		1.90 dd(15.3;8.0)
7-H	5.59 t(8.0)	5.53 t(7.8)	5.62 brt(8.4)	5.67 brt(8.0)	5.54 t(8.0)
9-H	4.32 d(10.0)	4.22 d(10.0)	6.29 d(10.9)	6.56 d(10.7)	6.15 d(10.7)
10-H	4.66 d(10.0)	4.60 d(10.0)	6.61 d(10.9)	6.76 d(10.7)	6.53 d(10.7)
13-H	4.57 t(7.3)	4.50 t(7.3)	5.70 brt(7.5)	5.71 brt(7.3)	4.47 t(7.1)
14-H	1.76 dd(14.8;6.9)	1.50 dd(14.9;7.0)	1.96 m	1.99 m	1.61 dd(15.1;7.1)
14'-H	2.30 dd(14.8;7.3)	2.13 m	2.42 dd(14.5;7.3)	2.46 dd(14.2;7.3)	2.25 dd(15.1;7.1)
16-Me	1.01 s	1.01 s	1.18 s	1.21 s	1.07 s
17-Me	1.03 s	1.07 s	1.18 s	1.21 s	1.17 s
18-Me	2.00 s	1.97 s	1.95 s	1.97 s	2.03 s
19-Me	2.11 s	2.02 s	1.76 s	1.87 s	1.68 s
20-H	4.17 d(8.0)	4.22 d(7.5)	4.16 d(7.9)	4.19 d(7.7)	4.39 d(7.6)
20'-H	4.56 d(8.0)	4.57 d(7.5)	4.48 d(7.9)	4.51 d(7.1)	4.51 d(7.6)
OAc	2.22 s	2.13 s	2.18 s	2.19 s	2.16 s
		2.01 s	2.16 s	2.16 s	2.08 s
			2.09 s	1.84 s	2.02 s
			1.76 s		1.75 s
OBz					
C-2*o*	8.02 d		8.02 d	8.04 d	
m	7.47 t		7.48 t	7.49 t	
p	7.61 t		7.61 t	7.61 t	
C-7*o*	8.06 d	8.05 d			
m	7.39 t	7.44 t			
p	7.52 t	7.56 t			
C-9*o*				7.64 d	
m				7.20 t	
p				7.35 t	
C-10*o*			7.87 d	7.76 d	7.85 d
m			7.43 t	7.24 t	7.42 t
p			7.56 t	7.36 t	7.55 t



871. $R^1 = R^2 = Bz$, $R^3 = R^4 = R^5 = H$

872. $R^1 = Ac$, $R^2 = Bz$, $R^3 = R^4 = R^5 = H$

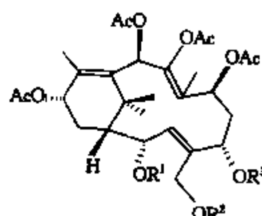
873. $R^1 = R^4 = Bz$, $R^2 = R^3 = R^5 = Ac$

874. $R^1 = R^3 = R^4 = Bz$, $R^2 = R^5 = Ac$

875. $R^1 = R^2 = R^3 = Ac$, $R^4 = Bz$, $R^5 = H$

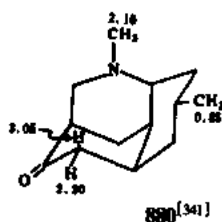
表 6-24 紫杉烷生物碱 876～879 的^{1}H-NMR 化学位移和偶合常数

质子\化合物	876	877	878	879
1β-H	1.79 m	1.75 dd(8.1,4.1)	1.75 m	1.74 m
2β-H	5.78 dd(11.5,4.6)	4.68 dd(10.4,2.2)	5.74 dd(11.5,4.8)	4.66 dd(10.8,4.2)
3-H	6.47 brd(11.5)	5.72 d(10.4)	6.22 dd(11.5,1.6)	6.27 brd(10.8)
5β-H	4.44 brs	5.54 brs	4.63 brs	4.53 brs
6α-H	2.00～2.03 m	2.00～2.02 m	2.00～2.03 m	2.02 m
6β-H	2.60 ddd(16.0,7.8,3.0)	2.60 ddd(16.5,8.9,2.0)	2.74 ddd(15.9,8.1,2.9)	2.63 m
7α-H	5.07 d(7.8)	5.39 brd(8.9)	5.01 d(8.1)	5.04 d(7.9)
10α-H	6.90 d(1.4)	7.12 s	6.89 d(1.2)	6.92 brs
13β-H	5.27 brd(9.2)	5.30 d(9.2)	5.27d(9.2)	5.31 d(9.4)
14α-H	2.16 brd(16.8)	2.00～2.02 m	2.25 brd(16.7)	2.02 m
14β-H	2.51 ddd(16.8,9.2,7.5)	2.52 ddd(15.7,9.2,7.9)	2.55 ddd(16.7,9.2,7.5)	2.49 m
16-Me	1.28 s	1.23 s	1.20 s	1.17 s
17-Me	1.11 s	1.08 s	1.12 s	1.13 s
18-Me	1.92 s	2.10 s	1.91 s	1.91 s
19-Me	1.63 d(1.4)	1.58 s	1.62 d(1.2)	1.60 s
20-Ha	4.81 d(12.8)	4.36 d(12.5)	4.55(12.7)	4.30 d(12.4)
20-Hb	4.35 d(12.8)	3.77 d(12.5)	3.45 d(12.7)	3.65 brd
2-OAc	2.00 s		2.00 s	
5-OAc		2.19 s	2.17 s	2.17 s
7-OAc	2.17 s	2.01 s	2.21 s	2.20 s
9-OAc	2.21 s	2.25 s	1.96 s	1.95 s
10-OAc	1.95 s	1.94 s	2.09 s	2.08 s
13-OAc	2.09 s	2.13 s		
20-OAc	2.01 s			
5-OH	3.90 brs			

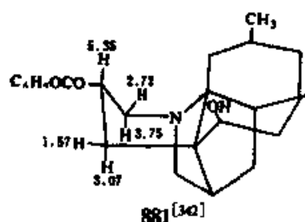


	R^1	R^2	R^3
876.	Ac	Ac	H
877.	Ac	H	H
878.	H	H	Ac
879.	H	H	H

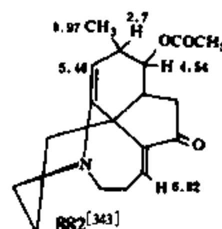
四、石松生物碱的^{1}H-NMR 化学位移



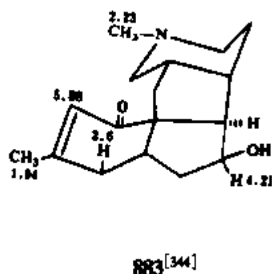
880[341]



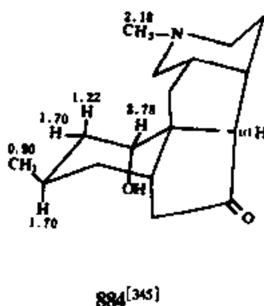
881[342]



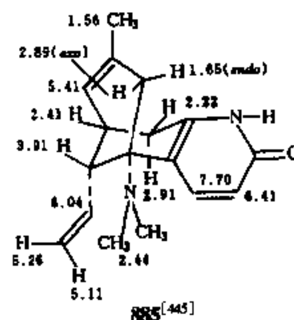
882[343]



883[344]



884[345]

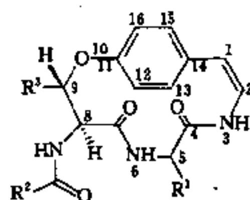


885[445]

第七节　环肽类生物碱的^{1}H-NMR化学位移和偶合常数

表 6-25　环肽生物碱 886～890 的^{1}H-NMR化学位移和偶合常数[458]

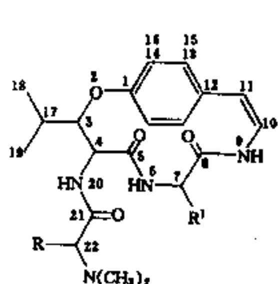
化合物 质子	886	887	888	889	890
1-H	6.01 brs	6.02 d(7.8)	6.50 m	6.70 d(7.4)	6.38 d(7.7)
2-H	6.43 d(7.2)	6.32 d(7.6)	6.66 m	6.20 m	—
3-H	6.00 m	—	5.96 d(9.6)	—	—
5-H	4.20 m	4.30 dd(9.2,6.7)	4.05 m	4.40 m	4.05 m
6-H	6.77～7.01 m		5.90 d(7.8)		
8-H	4.18 d(8.1)	4.60 m	4.69 dd(7.4,2)	4.66 m	4.65 m
9-H	4.64 d(7.9)	4.91 dd(6.6,1.9)	5.00 dd(7.4,2)	4.87 d(7.9)	4.92 dd(7.5,1.9)
12～16-H	6.77～7.01 m	7.38～7.54 m	7.00～7.50 m	7.00～7.50 m	7.05～7.50 m
17-H	1.40 m		1.38 d(7.3)	4.05 m	3.1 m
18-H	1.79 m	7.38～7.54 m		2.05 m	2.02 m
19-H	0.43 t(7.2)	—	0.59 d(6.5)	1.17 d(6.5)	0.57 d(6.6)
20-H	0.40 d(6.6)	—	0.73 d(6.5)	1.22 d(7.4)	1.14 d(6.8)
21-H	6.77～7.01 m	—	6.38 d(7.2)	—	—
23-H	3.54 t(1.8)	—	6.30 d(15.5)	3.44 t(1.8)	3.34 brd(14.8)
24-H			7.61 d(15.5)	3.04 d(2.0)	
26～30-H	6.77～7.01 m	3.39～3.55 m	7.00～7.50 m	7.00～7.50 m	7.00～7.50 m
31-H	—	—	—	—	—
32-H	2.42 s	6.68 d(15.4)	1.01 d(6.8)	2.88 s	2.85 s
33-H	2.42 s	7.72 d(15.4)	1.28 d(6.8)	2.91 s	2.97 s
34-H	1.8 m	—		2.05 m	2.05 m
35-H	0.73 d(6.6)	7.38～7.54 m		0.89 d(6.6)	0.71 d(6.6)
36-H	0.98 d(6.6)	—		0.76 d(6.6)	1.24 d(6.8)
37-H					
38-H					
39-H					
40-H		1.80m			
41-H		0.66 d(6.6)			
42-H		1.12 d(6.6)			



取代基 化合物	R¹	R²	R³	取代基 化合物	R¹	R²	R³
886	18 17 CH 19 20	26 25 29 30 32—N 31 33	35 34 CH 36	889	19 18 17 CH 20 OH	26 30 23 32—N 31 33	35 34 CH 36
887	20 19 18 17 CH₂ 23	35 34 39 31 O 27 N 26	41 40 CH 42	890	19 17 CH₂ 20 18	26 23 32—N 31 33	35 34 CH 36
888	19 CH₂ 20 18 17	26 25 24 30 23	32 31 CH 33				

表 6-26 环肽生物碱 891 ~ 894 的^{1}H-NMR 化学位移和偶合常数[459]

质子 \ 化合物	891	892	893	894
3-H	5.10 dd	4.80 dd	4.90 dd	4.80 dd
4-H	4.55 dd	4.40 dd	4.52 dd	4.44 dd
6-NH	5.80 dd	7.25 d	6.50 d	7.38 d
7-H	3.91 dd	3.90 dd	4.20 m	3.70 dd
9-NH	6.70 d	7.65 d	6.85 d	7.70 d
10-H	6.45 dd	6.20 dd	6.20 dd	6.15 dd
11-H	6.60 d	6.65 d	6.40 d	6.64 dd
13 ~ 16-H	7.08 ~ 7.30 m	6.80 ~ 7.00 dd	6.80 ~ 7.45 m	7.05 ~ 7.50 m
17-H	1.80 m	2.25 m	2.10 m, 1.25 d	2.20 m
18-H	1.30 d	0.90 d		1.10 d
19-H	1.05 d	1.10 d	1.05 d	1.25 d
20-NH	7.80 d	8.10 d	7.80 d	8.24 d
22-H	3.15 dd	2.75 d	2.63 d	3.40 dd
23-H	2.05 dd	1.70 d	1.80 d	2.95 d
24-H	6.80 ~ 7.40 m	1.50, 1.60 m	1.20, 1.55 m	10.78(NH)
25-H	6.80 ~ 7.40 m	0.80 t	0.90 t	6.80 ~ 7.30 m
26-H	6.80 ~ 7.40 m	0.65 d	0.75 d	6.80 ~ 7.30 m
27-H	6.80 ~ 7.40 m	1.28 m	2.90, 3.10 m	6.80 ~ 7.30 m
28-H	1.30 m	1.40 m	10.25 s	6.80 ~ 7.30 m
29-H	1.55 m	0.75 t	7.14 d	6.80 ~ 7.30 m
30-H	0.75 t	0.70 d		6.80 ~ 7.30 m
31-H	0.40 d		7.50 d	6.80 ~ 7.30 m
32-H			7.28 t	2.15 s
33-H			7.05 t	1.30, 1.74 m
34-H			7.40 d	1.80 m
35-H				0.60 d
36-H				0.62 d
N, *N*-二甲基	2.30 s	2.20 s	2.30 s	2.20 s



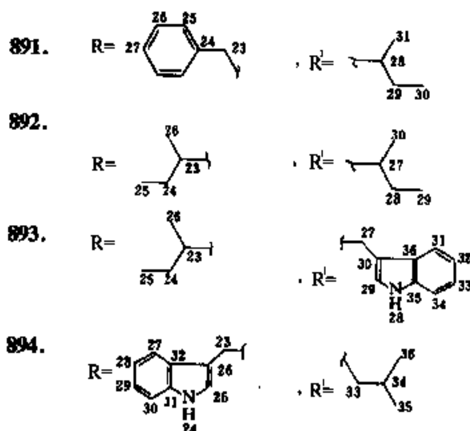
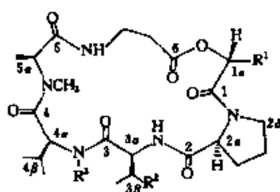


表 6-27 环肽生物碱 895,896 的^{1}H-NMR 化学位移和偶合常数[460]

质子 \ 化合物	895	896
Hia_1		
α-H	4.9 dd(10.1,3.3)	4.94 dd(9.7,3.7)
β-H	1.43 m,1.67 m	1.48 m,1.68 m
γ-H	1.75 m	1.77 m
δ-H	0.82 dd(6.5,0.8)	0.90 dd(8.9,5.7)
Pro_2		
α-H	4.33 d(8.3)	4.38 d(7.4)
β-H	1.98 m,2.13 m	2.05 m,2.13 m
γ-H	1.72 m	1.77 m
δ-H	3.40 m,3.86 t(9.3)	3.48 m,3.87 t(8.0)
Val_3		
NH	6.78 d(9.6)	6.98 d(9.3)
α-H	4.54 dd(9.6,5.2)	4.80 dd(9.3,5.8)
β-H	1.95 m	2.10 m
γ-H	0.76 d(6.8),0.84 d(6.5)	0.81 d(6.8),0.83 d(6.6)
Val_4		
NH/NCH_3	8.63 d(6.5)	3.13 s
α-H	4.27 dd(9.6,6.7)	4.92 d(10.9)
β-H	1.96 m	2.20 m
γ-H	0.79 d(6.8),0.98 d(6.8)	0.84 d(6.8),0.87 d(6.4)
Ala_5		
α-H	5.14 q(6.9)	5.15 q(6.7)
β-H	1.18 d(6.9)	1.17 d(6.7)
NCH_3	2.53 s	2.54 s
β-Ala_6		
NH	8.26 dd(9.3,3.5)	8.01 dd(9.3,3.5)
α-H	2.36 m,2.69 m	2.38 m,2.70 m
β-H	3.00 br t(11.3),3.79 m	2.92 t(11.2),3.83 m

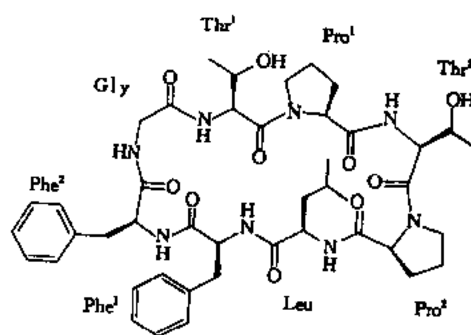


895. $R^1 = CH_2CH(CH_3)_2$, R^2 = H, R^3 = H

896. $R^1 = CH_2CH(CH_3)_2$, R^2 = H, $R^3 = CH_3$

表 6-28 环肽生物碱 897 的^{1}H-NMR 化学位移和偶合常数[461]

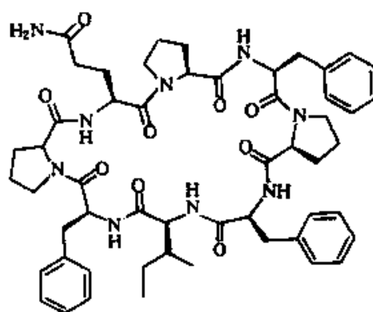
化合物 质子	897	化合物 质子	897	化合物 质子	897
Gly		Thr^2		Phe^1	
α	3.79 dd(6.5,16.9)	OH	4.94 d(6.6)	α	4.82 m
NH	8.84 brs	NH	8.05 brs	β	2.81 dd(10.0,13.5)
C=O		C=O			2.75 dd(3.4,13.5)
Thr^1		Pro^2		γ	
α	4.90 brd(6.1)	α	4.13 t(7.5)	δ	7.19 m
β	4.28 m	β	2.09 m	ε	7.29 m
γ	0.98 d(6.3)		1.76 m	ζ	7.16 m
OH	5.40 d(12.0)	γ	1.86 m	NH	7.33 d(9.4)
NH	7.46 brs	δ	3.83 m	C=O	
C=O			3.69 m	Phe^2	
Pro^1		C=O		α	4.19 ddd(4.1,6.7,7.6)
α	4.49 dd(4.9,8.4)	Leu		β	2.96 dd(8.3,14.0)
β	2.07 m	α	3.58 ddd(4.3,6.9,11.0)		2.88 dd(6.7,14.0)
	1.98 m	β	1.66 ddd(4.3,11.0,13.7)	γ	
γ	1.83 m		1.13 m	δ	7.28 m
δ	3.67 m	γ	1.35 m	ε	7.18 m
C=O		δ	0.79 d(6.6)	ζ	7.22 m
Thr^2			0.71 d(6.6)	NH	8.84 brs
α	4.59 dd(7.4,8.3)	NH	7.65 d(6.9)	C=O	
β	3.97 m	C=O			
γ	1.14 d(6.2)				



897

表 6-29 环肽生物碱 898 的^{1}H-NMR 化学位移和偶合常数[462]

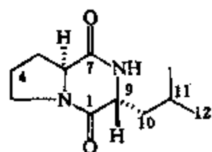
化合物 / 质子	898
Pro^5	
CO	
α-CH	2.86
β-CH_2	0.71 m,1.65
γ-CH_2	0.50 m,1.32
δ-CH_2	2.87,3.12
Phe^6	
NH	8.72 d(8.8)
CO	
α-CH	4.23 ddd (3.3,8.8,12.1)
β-CH_2	2.92 t(12.1)
1-C	
2,6-CH	7.24
3,5-CH	7.19
4-CH	7.10
ile^7	
NH	7.46 d(8.8)
CO	
α-CH	4.07 d(7.7)
β-CH	1.65
β-CH_3	1.07 d(6.7)
γ-CH_2	1.17,1.57
ile^7	
δ-CH_3	0.88 t(7.2)
Phe^8	
NH	8.43
CO	
α-CH	4.38
β-CH_2	2.84,3.14
1-C	
2,6-CH	7.17~7.20
3,5-CH	7.20~7.36
4-CH	7.29~7.33
Pro^1	
CO	
α-CH	2.85
β-CH_2	0.94,1.81
γ-CH_2	1.35,1.58
δ-CH_2	3.30
gln^2	
NH	8.67 d(8.1)
CO	
α-CH	4.16 brt(11.2)
β-CH_2	1.88,1.94
γ-CH_2	2.00,2.10
γ-CO	
NH_2	6.62 brs,7.20
Pro^3	
CO	
α-CH	4.36
β-CH_2	1.91,2.13
γ-CH_2	1.83,1.91
δ-CH_2	3.46 td(4.2,10.1)
	3.66 td(4.3,10.1)
Phe^4	
NH	8.45
CO	
α-CH	4.37
β-CH_2	2.85
	3.07 dd(4.4,12.5)
1-C	
2,6-CH	7.17~7.20
3,5-CH	7.20~7.36
4-CH	7.29~7.33



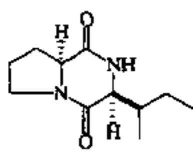
898

表 6-30　环肽生物碱 899 ~ 904 的¹H-NMR 化学位移和偶合常数[463]

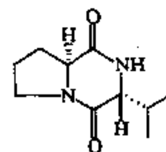
化合物 / 质子	899	900	901	902	903	904
3-H	3.6 ~ 3.5 m	3.6 ~ 3.5 m	3.55 dt	3.52 dt	3.69 dt	3.7 ~ 3.6 m;
			(9.1,2.8)	(9.8,2.7)	(8.3,3.9)	3.6 ~ 3.5 m
			3.63 m	3.62 dt	3.53 dt	
				(9.0,4.5)	(10.4,2.1)	
4-H	1.94 ~ 1.86 m;	2.0 ~ 1.9 m;	2.02 ~ 1.99 m;	1.96 m	1.90m	1.9 ~ 1.8 m
	2.02 ~ 1.99 m	1.9 ~ 1.8 m	1.93 ~ 1.88 m	1.88 m		
5-H	2.13 m;	2.3 ~ 2.2 m;	2.4 ~ 2.3 m;	2.37 ddd	2.40 ddd	2.4 ~ 2.3 m;
	2.33 m	2.1 ~ 2.0 m	2.1 ~ 2.06 m	(8.7,6.4,2.4);	(10.8,6.3,4.3);	2.1 ~ 2.0 m
				2.02 m	1.98 m	
6-H	4.12 t(8.1)	4.07 t(7.5)	4.08 dt	4.07 dd	4.08 dt	4.08 t(7.1)
			(7.8,1.8)	(6.9,1.5)	(9.5,3)	
N-H	5.91 brs	5.99 brs	5.72 dd	6.68 brs	6.31, brd(1.5)	5.60 brs
			(1.5,1.2)			
9-H	4.01 dd	3.96 brs	3.94 brs	3.92 ddd	3.77 dt	4.27 dd
	(9.4,3.4)			(9.9,5.4,4.5)	(5.1,1.8)	(10.6,2.6)
10-H	2.01 m;	2.4 ~ 2.3 m	2.64 m	1.75 q(6.3)	2.04 m;	3.6 ~ 3.5 m;
	1.52 ddd			1.63 ddd	1.83 m	2.77 dd
	(14.5,9.6,4.9)			(11.1,6.5,1.8)		(14.4,10.8)
11-H	1.76 ~ 1.69 m	1.5 ~ 1.4 m;	0.91d(7.2)	1.66 ~ 1.60 m	1.54 m;	
		1.3 ~ 1.1 m		(H-10)	1.23 m	
12-H	0.94 d(6.3)	0.92 t(7.4)		0.94 d(6.3)	0.92 t(7.3)	
Me11	1.00 d(6.3)			0.97 d(6.3)		
Me10		1.06 d(7.2)	1.06 d(7.2)			
Me4					1.01 d(6.9)	
Ar10						7.4 ~ 7.2



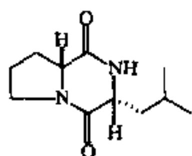
899



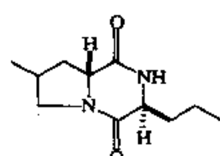
900



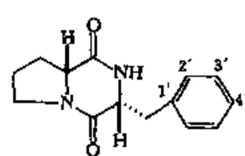
901



902



903



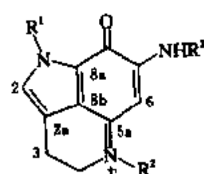
904

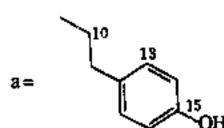
第八节 其他类型生物碱的^{1}H-NMR 化学位移和偶合常数

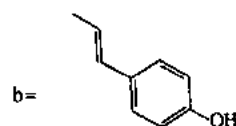
表 6-31 吡咯醌型生物碱 905 ~ 908 的^{1}H-NMR 化学位移和偶合常数①[464]

化合物 / 质子	905		906		907		908	
2-H	7.31	s	7.33	s	7.28	s	7.33	s
2a-H								
3-H	2.91	t(7.5)	2.84	t(7.5)	2.93	t(7)	2.89	t(7)
4-H	3.89	t(7.5)	3.78	t(7.5)	3.92	t(7)	3.87	t(7)
5a-H								
6-H	5.59	s	5.47	s	6.28	s	6.12	s
7-H								
8-H								
8a-H								
8b-H								
10-H	3.59	m	3.48	m	7.58	m	6.99	d(13.5)
11-H	2.81	t(7)	2.77	t(7)	7.05	d(13.5)	7.40	d(13.5)
12-H								
13,17-H	7.04	d(8)	7.03	d(8)	7.41	d(8)	7.38	d(8)
14,16-H	6.68	d(8)	6.68	d(8)	6.76	d(8)	6.77	d(8)
15-H								
1-NH	13.09	brs			13.10	brs	13.12	brs
1-NMe			3.89	s(3H)				
5-NH			10.47	brs			10.63	brs
5-NMe	3.37	s(3H)			3.47	s(3H)		
9-NH	9.13	t(6)	8.97	t(6)	10.78	d(11)	10.63	brs
OH	9.1	brs	9.3	brs	9.8	brs	9.8	brs

① 括号内为 J 值。



a=


b=


	R^1	R^2	R^3
905.	H	Me	a
906.	Me	H	a
907.	H	Me	b
908.	H	H	b

表 6-32 哒嗪生物碱 909 ~ 912 的^{1}H-NMR 化学位移和偶合常数[465]

化合物 / 质子	909	910	911	912
2-H				4.24 m
5-H				3.67 q(5.3)
7-H	5.88 s	5.13 s	5.12 s	3.13 dd(4.4,14.6)
				3.45 dd(3.9,14.6)
9-H	7.41 d(7.2)	7.38 d(7.3)	7.35 d(6.6)	7.06 s
10-H	7.28 m	7.26 m	7.27 m	
11-H	7.21 m	7.20 m	7.22 m	
12-H	7.28 m	7.26 m	7.27 m	
13-H	7.39 d(7.2)	7.38 d(7.3)	7.35 d(6.6)	6.85 brd(6.7)
14-H	3.27 m	2.00 m	1.43 m	6.92 dd(7.2,7.7)
15-H	1.20 d(5.6)	0.74 d(7.7)	−0.19 d(6.9)	7.44 brd(7.0)
16-H	1.22 d(5.6)	0.90 d(6.8)	0.68 d(6.8)	
17-H	3.84 s	3.77 s	3.81 s	3.51 d(7.4)
18-H		1.97 s	3.05 s	5.21 t(7.2)
20-H				1.71 s
21-H				1.71 s
22-H				0.35 d(7.1)

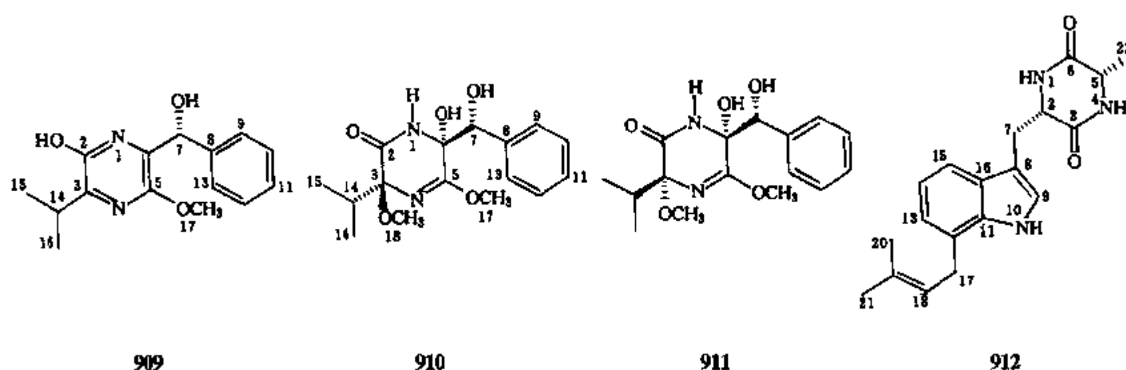
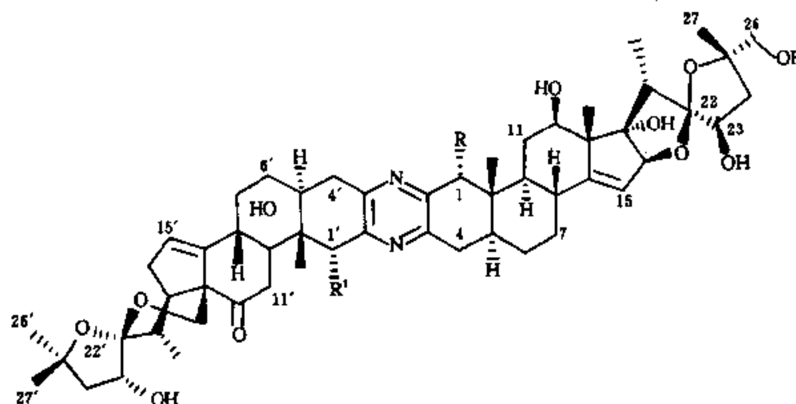


表 6-33 双甾体生物碱 913 的 ^{1}H-NMR 化学位移和偶合常数[466]

质 子	913 左侧		质 子	913 右侧	
	δ	nOe		δ	nOe
1α-H	3.74	5α-H,9-OH	1-OMe	3.50	9α-H,11α-H,1β-H
1β-H	2.99	19-Me	1β-H	4.15	19-Me,11α-H,1α-OMe
4α-H	3.06	5α-H,6α-H	4α-H	3.00	5α-H
4β-H	2.73	6β-H	4β-H	2.61	6β-H,19-Me
5α-H	2.55	1α-H,4α-H,6α-H	5α-H	2.27	4α-H,6α-H,9α-H
6α-H	1.70	4α-H,5α-H,7β-H	6α-H	1.52	4α-H,5α-H,7α-H
6β-H	1.48	4β-H,8β-H,19-Me	6β-H	1.28	4β-H,7β-H,19-Me
7α-H	2.02	15-H	7α-H	1.34	5α-H,9α-H,15-H
7β-H	1.90	15-H	7β-H	1.64	15-H
8β-H	2.75	6β-H,11β-H,18-H,19-Me	8β-H	2.13	6β-H,7β-H,11β-H,18-Me,19-Me
9-OH	5.97	1α-H,11α-H,5α-H	9α-H	1.86	11α-H,12α-H,5α-H
11α-H	2.96		11α-H	2.12	12α-H,9α-H,1β-H
11β-H	3.31	8β-H,18-H,19-Me	11β-H	1.85	8β-H,18-Me,19-Me
15-H	5.57	7α-H,7β-H,16β-H,16α-H	12α-H	4.24	9α-H,11α-H
16α-H	2.27	21-H	15-H	5.62	7α-H,7β-H
16β-H	2.92	15-H,21-Me	16α-H	5.24	15-H,17-OH



913. R = OMe, R^1 = H

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464 Schmidt E W et al. J Nat Prod, 1995; 58: 1861
465 Wang Y et al. J Nat Prod, 1995; 58: 93
466 Pettit G R et al. J Nat Prod, 1995; 58: 52

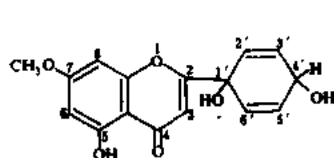
第七章　黄酮类化合物的^{1}H-NMR 化学位移和偶合常数

第一节　黄酮及黄酮醇类化合物的^{1}H-NMR 化学位移及偶合常数

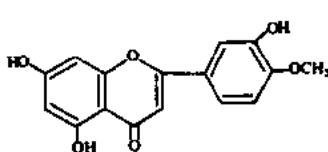
一、黄酮化合物的^{1}H-NMR 化学位移

表 7-1　黄酮化合物 1～9 的^{1}H-NMR 化学位移[1,2]

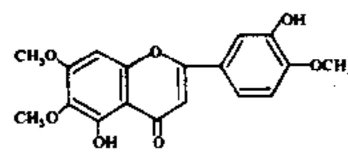
质子＼化合物	1	2	3	4	5	6	7	8	9
3-H	6.44s	6.55s	6.30s	—	—	6.62s	6.55s	6.55s	6.60s
6-H	6.42d(2.5)	6.22	—	—	—	—	—	—	—
8-H	6.62d(2.5)	6.46d	6.56d	6.54d	6.48d	—	—	—	—
2′-H	5.92d(10)	7.40d(2.5)	7.26d(2.5)	7.60d(2.5)	7.56d(2.5)	7.16s	7.05d(1.5)	7.34d(1.5)	7.40d(1.5)
3′-H	6.20dd(10,4)	—	—	—	—	—	—	—	—
5′-H	6.20dd(10,4)	7.10d(9)	6.88d(9)	6.84d(9)	6.88d(9)	—	—	6.90d(8.5)	6.97d(8.5)
6′-H	5.92d(10)	7.5dd(9)	7.40dd (9,2.5)	7.70dd (9,2.5)	7.60dd (9,2.5)	7.16s	7.15d(1.5)	7.48dd (8.5,1.5)	7.55dd (8.5,1.5)
3-OCH$_3$	—	—	—	—	3.88s	—	—	—	—
4′-OCH$_3$	—	3.97s	3.72s	3.87s	3.72s	3.95s (12H)	3.94s (6H)	3.94s (6H)	3.95s (12H)
7-OCH$_3$	3.92s	—	3.88s	—	—	3.92s	4.00s (6H)	4.00s	4.01s
6-OCH$_3$	—	—	3.96s	3.72s	3.94s	4.09s(6H)	4.08s	4.09s	4.09s
O—CH$_2$—O	—	—	—	—	—	—	6.06s	6.05s	—
5-OH	12.79s	—	—	—	—	—	—	—	—
1′-OH	6.26s	—	—	—	—	—	—	—	—
4′-OH	4.46bs	—	—	—	—	—	—	—	—



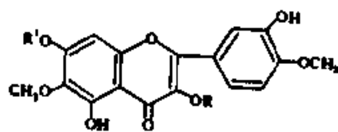
1



2

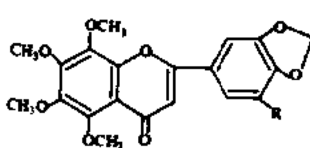


3



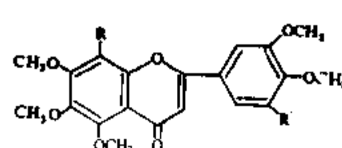
4. R = R^1 = H

5. R = R^1 = CH$_3$



7. R = OCH$_3$

8. R = H

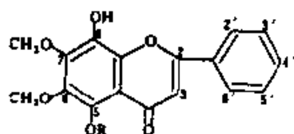


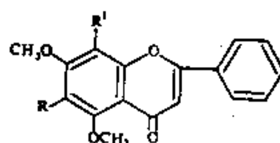
6. R = R^1 = OCH$_3$

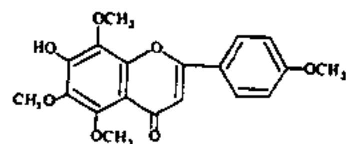
9. R = OCH$_3$, R^1 = H

表 7-2 黄酮化合物 10～18 的 ^{1}H-NMR 化学位移[3]

质子 \ 化合物	10	11	12	13	14	15	16	17	18
3-H	6.69s	6.70s	6.70s	6.70s	6.73s	—	6.66s	6.73s	—
6-H	—	—	—	6.39d	—	—	—	—	—
8-H	—	—	—	6.59d	—	6.45s	—	—	6.80s
2′,6′-H	7.94m	7.93m	7.94m	7.88m	7.88d	8.11m	7.90m	7.93m	8.10m
3′,5′-H	7.56m (3′,5′,4′-H)	7.52m	7.54m	7.60m	7.03d	7.55m	7.54m	7.53m	7.55m
4′-H					—				
OCH_3	4.05s	4.07s	4.12s	3.97s	4.07s	4.01s	4.06s	4.06s	4.00s
	4.03s	4.03s	4.04s	3.93s	4.04s	3.88s	3.88s	3.96s	3.86s
	—	3.96s	3.95s	—	3.95s	—	—	3.94s	—
					3.79s				
$OCOCH_3$	— —	— —	— —	—	—	—	2.48s	2.43s	2.43s
	—	—	—	—	—	—	2.43s	—	2.38s
OH	12.71s	—	—	—	—	12.38s	—	—	—







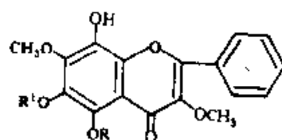
10. R = H

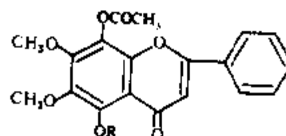
11. R = CH_3

12. R = R^1 = OCH_3

13. R = R^1 = H

14



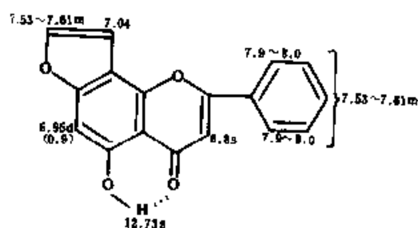


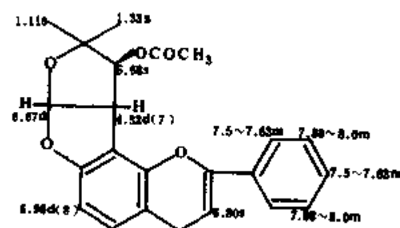
15. R = H, R^1 = $COCH_3$

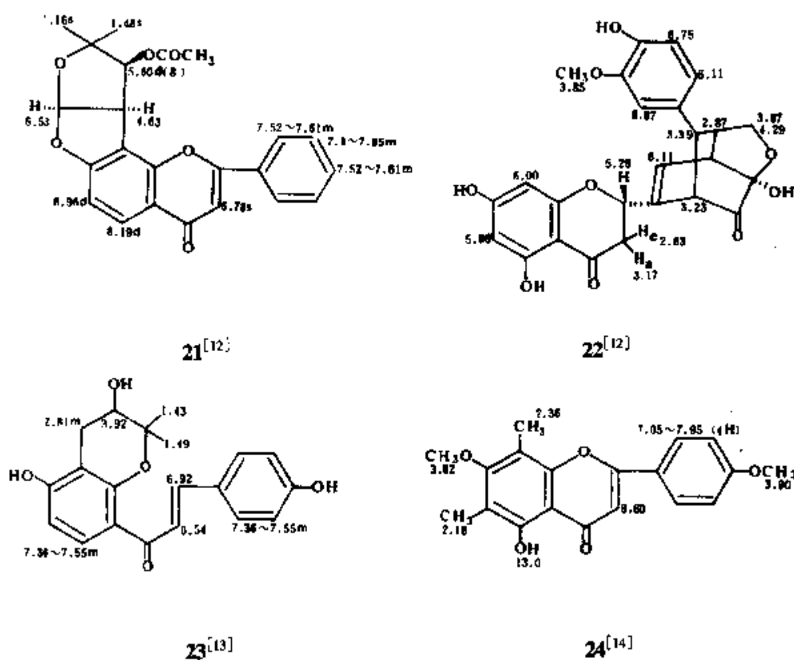
18. R = $COCH_3$, R^1 = $COCH_3$

16. R = $COCH_3$

17. R = CH_3







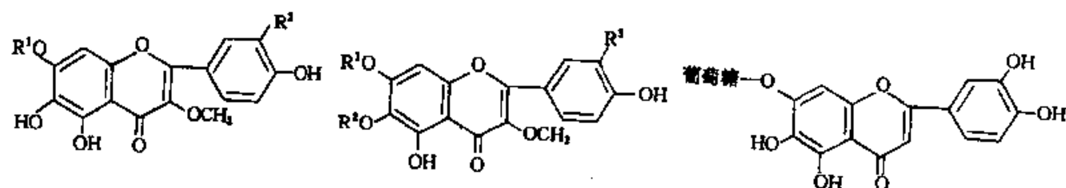
21[12]　22[12]

23[13]　24[14]

二、黄酮醇类化合物的^{1}H-NMR化学位移

表 7-3　黄酮醇化合物 25～34 的^{1}H-NMR化学位移[4]

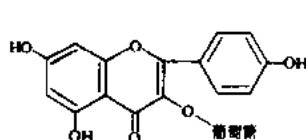
质子 \ 化合物	25	26	27	28	29	30	31	32	33	34
2′-H	7.92d (9.0)	7.60d (2.5)	7.6d (2.5)	7.28d (2.5)	7.95d (9.0)	7.95d (9.0)	7.95d (9.0)	7.6d (2.5)	7.55d (9.0)	7.55d (2.5)
6′-H	7.92d (9.0)	7.5dd (2.5)(9.0)	7.5dd (2.5)(9.0)	7.35dd (2.5,9.0)	7.95d (9.0)	7.95d (9.0)	7.95d (9.0)	7.45dd (2.5,9.0)	7.55d (9.0)	7.6dd (2.5,9.0)
5′-H	6.87d (9.0)	6.83d (9.0)	6.82d (9.0)	6.84d (9.0)	6.9d (9.0)	6.9d (9.0)	6.85d (9.0)	6.8d (9.0)	6.85d (9.0)	6.8d (9.0)
3′-H	6.87d (9.0)	—	—	—	6.9d (9.0)	6.9d (9.0)	6.85d (9.0)	—	6.85d (9.0)	—
6-H	—	—	—	—	—	—	6.2d (2.0)	—	—	—
8-H	6.50s	6.50s	6.50s	6.60s	6.50s	6.45s	6.30d (2.0)	6.55d	6.50s	6.6s
3-H	—	—	—	6.35s	—	—	—	—	—	—
1″-H	—	—	—	5.02d (8.0)	—	5.05d (7.0)	5.78d (7)	5.05m	5.1m	5.0m
2″～6″-H	—	—	—	3.3～3.8m	—	3.3～3.8m	3.3～3.75m	3.35～3.8m	3.2～3.8m	3.3～3.76m
3-OCH$_3$	3.90s	3.90s	3.85s	—	3.84s	3.9s	—	3.86s	3.85s	—
6-OCH$_3$	—	—	3.75s	—	—	—	—	—	—	3.75s
7-OCH$_3$	3.83s	3.85s	—	—	—	—	—	—	—	—



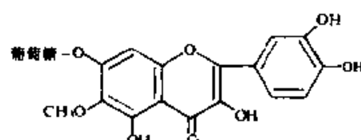
25. $R^1 = CH_3, R^2 = H$
26. $R^1 = CH_3, R^2 = OH$
29. $R^1 = R^2 = H$
32. R^1 = 葡萄糖基, $R^2 = OH$
33. R^1 = 葡萄糖基, $R^2 = H$

27. $R^1 = H, R^2 = CH_3, R^3 = OH$
30. $R^1 = R^3 = H$, R^2 = 葡萄糖基

28



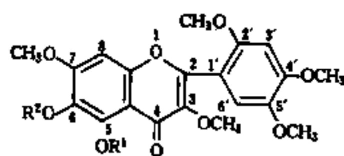
31



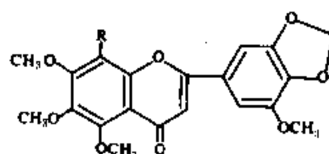
34

表 7-4 黄酮醇化合物 35～43 的 ^1H-NMR 化学位移[5]

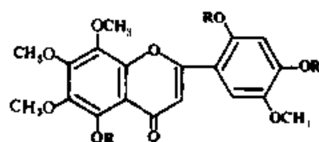
质子 \ 化合物	35	36	37	38	39	40	41	42	43
2-H	—	—	—	—	5.26dd	5.30dd	—	—	—
3-H	—	—	—	—	2.70dd 2.98dd	2.7～3.2m	6.58	6.59	—
8-H	6.83s	6.47s	6.48s	6.71s	6.32s	—	—	—	—
2′-H	—	—	—	—	6.62br	6.61br	—	—	—
3′-H	6.62s	6.62s	6.63s	6.76s	—	—	7.04	7.15	—
6′-H	6.94s	6.96s	6.99s	7.06s	6.62br	6.61br	7.54	7.42	—
5-OH	—	12.71s	12.47s	—	—	—	—	—	—
OCH_3	3.95	3.96	3.96	4.06	3.80	3.82	3.96	3.82	3.87(3-)
	3.89	3.86	3.94	4.00	3.86	3.86	3.97	3.84	3.96(5-)
	3.85	3.86	3.86	3.96	3.92	3.90	3.98	3.94	3.94(6-)
	3.83	3.84	3.86	3.93	—	4.03	4.03	4.03	4.09(7-)
	3.70	3.78	3.77	3.91×2	—	—	4.11	—	3.98(8-)
$-OCH_2-O-$	—	—	—	—	5.96s	5.95s	—	—	—
$OCOCH_3$	2.45	2.37	—	—	—	—	—	—	—
	2.33	—	—	—	—	—	—	—	—



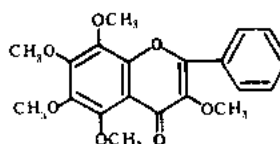
35. $R^1 = R^2 = COCH_3$
36. $R^1 = H, R^2 = COCH_3$
37. $R^1 = R^2 = H$
38. $R^1 = R^2 = CH_3$



39. R = H
40. $R = OCH_3$



41. $R = CH_3$
42. R = H

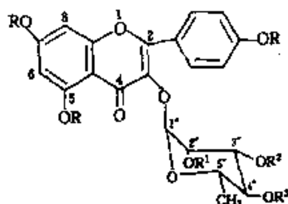


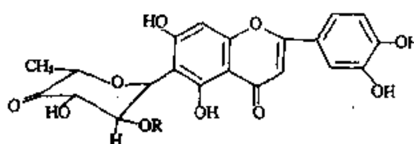
43

表 7-5 黄酮醇化合物 44 ~ 47 的 ^{1}H-NMR 化学位移[6,7]

质子 \ 化合物	44	45	46	47
3-H	—	—	6.48s	6.45s
6-H	6.29d(2)①	6.99d(2)	—	—
8-H	6.48d(2)	7.15d(2)	6.50s	6.48s
2′,6′-H	7.87d(9)	8.07d(9)	7.33(AB)	7.30
3′,5′-H	7.07d(9)	7.39d(9)	6.87(X)	6.85
1″-H	5.57d(1.2)	5.57d(1.3)	5.34d(9)	5.26d(9)
2″-H	4.43br	5.64dd(1.5,2)	4.75t(9)	4.62t(9)
3″-H	5.18dd(3,10)	5.21dd(2,9)	4.40bd(9)	4.30d(9)
4″-H	5.08dd(9,10)	4.89dd(9,9)	—	—
5″-H	3.50dq(6,9)	3.30dd(6,9)	4.22q(6)	4.23q(6)
6″-H	0.83d(6)	0.82d(6)	1.26d(6)	1.28d(6)
1‴-H	—	—	5.16d(2)	—
2‴-H	—	—	3.77dd(2)	—
3‴-4‴-H	—	—	3.0 ~ 3.5m	—
5‴-H	—	—	2.60dq(6,9)	—
6‴-H	—	—	0.78d(6)	—
5-OH	12.65br	—	—	—
7-OH	9.4br	—	—	—
4′-OH	9.4br	—	—	—

① 括号内的数字表示偶合常数。





44. R = R^{1} = H, R^{2} = R^{3} = COCH$_3$

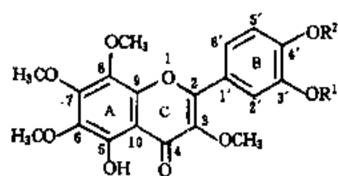
45. R = R^{1} = R^{2} = R^{3} = COCH$_3$

46. R = α-鼠李糖基

47. R = H

表 7-6 黄酮醇化合物 48 和 49 的 ^{1}H-NMR 化学位移[26]

质子 \ 化合物	48		49	
	CDCl$_3$	C$_6$D$_6$	CDCl$_3$	C$_6$D$_6$
2′-H	7.77,d(2.2)	8.03,d(2.2)	7.80,s	7.61,d(2.0)
5′-H	7.00,d(7.0)	6.37,d(8.7)	7.07,d(7.5)	7.00,d(8.6)
6′-H	7.78,dd(2.2,7.0)	7.79,dd(2.2,8.7)	7.78,dd(1.5,7.5)	7.80,dd(2.0,8.6)
5-OH	12.40,s	13.12,s	12.39,s	13.15,s
3′-OH	5.73,s	5.41,s	—	—
4′-OH	—	—	6.02,s	5.66,s
3′-OMe	—	—	3.98,s	3.21,s
4′-OMe	4.00,s	3.07,s	—	—
3-OMe	3.88,s	3.84,s	3.88,s	3.85,s
6-OMe	3.95,s	3.81,s	3.95,s	3.82,s
7-OMe	4.11,s	3.72,s	4.11,s	3.69,s
8-OMe	3.96,s	3.65,s	3.96,s	3.64,s



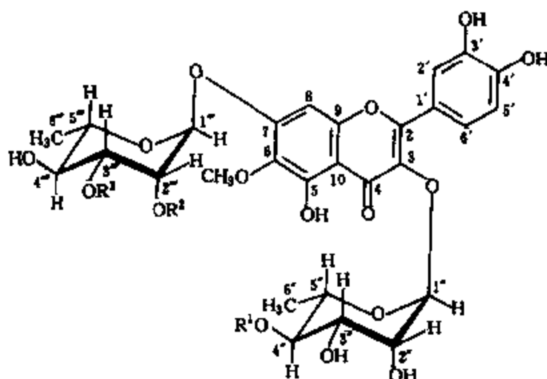
48. $R^1 = H, R^2 = CH_3$

49. $R^1 = CH_3, R^2 = H$

表 7-7 黄酮醇化合物 50～55 的 ^{1}H-NMR 化学位移①[27]

化合物 / 质子	50	51	52	53	54	55
6-OCH₃	3.90s	3.93s	3.90s	3.88s	3.93s	3.88s
8-H	6.63s	6.66s	6.62s	6.65s	6.65s	6.64s
2′-H	7.38d(2.1)	7.39d(2.3)	7.42d(2.1)	7.38d(2.1)	7.40d(2.0)	7.42d(2.0)
5′-H	6.92d(8.3)	6.94d(8.2)	6.93d(8.1)	6.93d(8.4)	6.93d(8.5)	6.93d(8.2)
6′-H	7.35dd(8.3,2.1)	7.35dd(8.2,2.3)	7.39dd(8.1,2.1)	7.33dd(8.4,2.1)	7.39dd(8.5,2.0)	7.39dd(8.2,2.0)
3-*O*-Rha						
1″-H	5.50d(1.6)	5.51brs	5.37d(1.7)	5.50d(1.6)	5.37brs	5.37brs
2″-H	4.22dd(3.3,1.6)	4.23brs	4.23dd(3.2,1.7)	4.22dd(3.4,1.6)	4.24brs	4.24brs
3″-H	3.90dd(9.5,3.3)	3.92dd(9.0,3.0)	3.77dd(9.2,3.2)	3.90dd(9.9,3.4)	3.78dd(8.5,3.0)	3.77dd(9.5,3.3)
4″-H	4.82dd(9.5,9.5)	4.86m	3.34dd(9.2,9.2)	4.82dd(9.9,9.9)	3.33dd(8.5,8.5)	3.35dd(9.5,9.5)
5″-H	3.34dq(9.5,6.2)	3.34m	3.45dq(9.2,6.1)	3.34dq(9.9,6.3)	3.45m	3.45m
6″-CH₃	0.79d(6.2)	0.80d(6.1)	0.95d(6.1)	0.79d(6.3)	0.96d(6.1)	0.95d(6.1)
4″-OAc	2.04s	2.05s	—	2.04s	—	—
7-*O*-Rha						
1‴-H	5.61d(1.7)	5.59brs	5.61d(1.7)	5.57d(1.6)	5.58brs	5.57brs
2‴-H	5.29dd(3.6,1.7)	4.27brs	5.29dd(3.6,1.7)	4.10dd(3.5,1.6)	4.27brs	4.11brs
3‴-H	4.08dd(9.6,3.6)	5.20dd(9.5,3.5)	4.08dd(9.4,3.6)	3.88dd(9.5,3.5)	5.20dd(9.3,3.2)	3.90dd(9.5,3.5)
4‴-H	3.46dd(9.6,9.6)	3.71dd(9.5,9.5)	3.47dd(9.4,9.4)	3.50dd(9.5,9.5)	3.72dd(9.3,9.3)	3.50dd(9.5,9.5)
5‴-H	3.73dq(9.6,6.4)	3.75m	3.73dq(9.4,6.1)	3.65dq(9.5,6.1)	3.65m	3.66dq(9.5,6.1)
6‴-CH₃	1.27d(6.4)	1.29d(5.5)	1.27d(6.1)	1.26d(6.1)	1.28d(5.6)	1.26d(6.1)
2‴-OAc	2.15s	—	2.15s	—	—	—
3‴O-Ac	—	2.16s	—	—	2.16s	—

① 括号内数据为偶合常数。



50. $R^1 = R^2 = Ac,\ R^3 = H$

51. $R^1 = R^3 = Ac,\ R^2 = H$

52. $R^2 = Ac,\ R^1 = R^3 = H$

53. $R^1 = Ac,\ R^2 = R^3 = H$

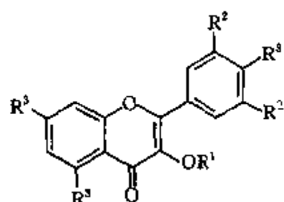
54. $R^3 = Ac,\ R^1 = R^2 = H$

55. $R^1 = R^2 = R^3 = H$

表 7-8　黄酮醇化合物 56 ~ 59 的^{1}H-NMR 化学位移[28]①

质子 \ 化合物	56	57	58	59
6-H	6.17d(1.8)	6.19d(1.8)	6.18d(1.8)	6.19d(2.0)
8-H	6.36d(1.5)	6.37s	6.38d(2.1)	6.37d(1.8)
2'-H	7.92d(8.7)	7.52d(2.1)	8.05d(9.0)	7.12s
3'-H	6.89d(9.0)	—	6.87dd(2.1,8.7)	—
5'-H	6.89d(9.0)	6.89d(8.4)	6.87dd(2.1,8.7)	—
6'-H	7.92d(8.7)	7.48dd(1.6,8.4)	8.04d(9.0)	7.12s
1''-H	5.46s	5.46s	5.23d(7.5)	5.45s
2''-H	4.30d(3.0)	4.33d(2.7)	3.40dd(7.2,10.0)	4.34s
3''-H	3.89dd(3.0,5.1)	3.89dd(2.7,4.8)	3.25 ~ 3.40m	3.91d(1.2)
4''-H	3.79dd(4.2,8.9)	3.80dd(4.8,9.6)	3.25 ~ 3.40m	3.91d(1.2)
5''-H	3.47d(4.0)	3.30dd(3.3,1.5)	3.20ddd(2.1,5.1,7.5)	3.51d(1.2)
6''-H	—	—	3.50dd(5.4,11.7)	—
			3.71dd(2.1,11.7)	

① 括号内为偶合常数。



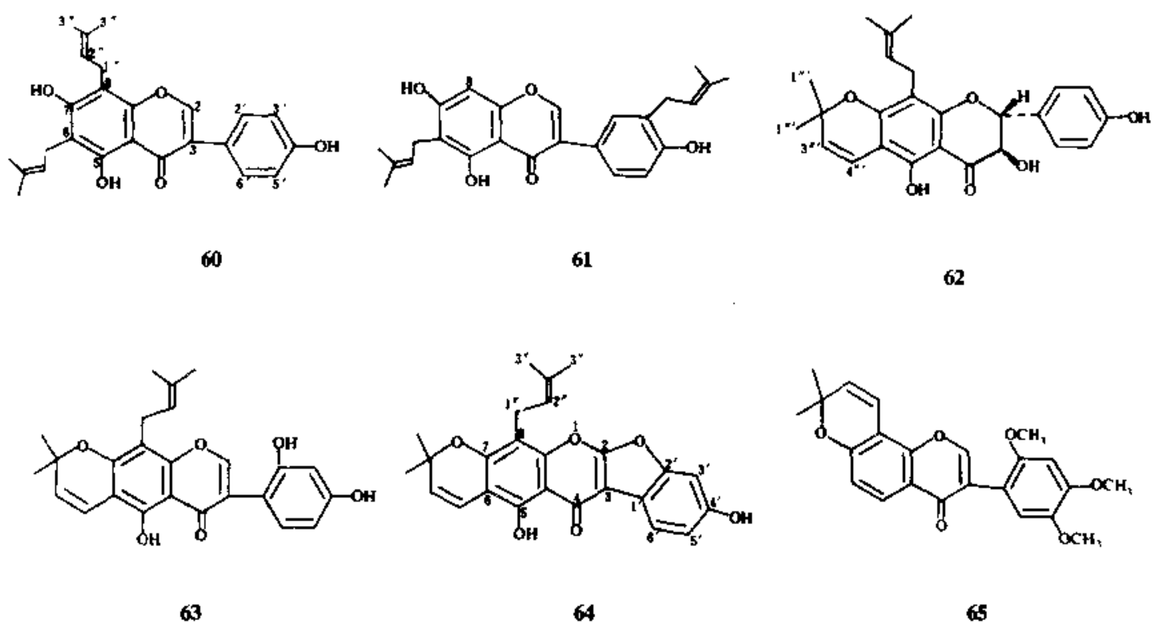
56. R¹ = α-L-Arafur，R² = R²' = H，R³ = OH
57. R¹ = α-L-Arafur，R²' = H，R² = R³ = OH
58. R¹ = β-D-Glu，R² = R²' = H，R³ = OH
59. R¹ = α-L-Arafur，R² = R²' = R³ = OH

三、异黄酮类化合物的^{1}H-NMR 化学位移

表 7-9　异黄酮化合物 60 ~ 65 的^{1}H-NMR 化学位移[8,9,10]①

质子 \ 化合物	60	61	62	63	64	65
2-H	7.88	7.82	4.49d(12)	8.30	—	7.96s
3-H	—	—	4.99t(12)	—	—	—
6-H	—	—	—	—	—	6.84d(9)
8-H	—	6.38s	—	—	—	—
2'-H	7.32d(8)	—	7.41d(8)	—	—	—
3'-H	6.80d(8)	—	6.86d(8)	6.45 ~ 6.65m	6.82d(2)	6.62s
5'-H	6.80d(8)	6.85d(8)	6.86d(8)	—	7.02q(8,2)	—
		7.25dd(8)				
6'-H	7.32d(8)	7.20d(2)	7.41d(8)	7.25d(8)	7.65d(8)	6.97s
5-OH	13.08	13.18	11.37	—	—	8.06d(9)
1''-H	3.46m	3.38m	3.16d(7.5)	3.46d(7)	3.30d(7)	—
2''-H	5.24m	5.38 + (7)	5.11 ± (7.5)	5.36m	5.15m	—
3''-H	1.83 × 2	1.82 × 2	1.63	1.65	1.65	—
	1.77 × 2		1.59	1.85	1.85	
1'''-H	—	—	1.44	1.49s	1.45s	1.48
3'''-H	—	—	5.51d(10)	5.85d(10)	5.75d(10)	5.68d(10)
4'''-H	—	—	6.63d(10)	6.75d(10)	6.60d(10)	6.82d(10)

① 括号内数字表示偶合常数。

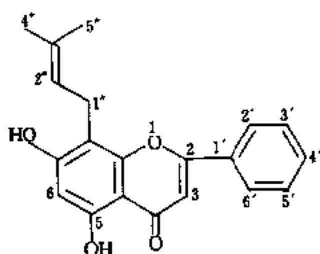


第二节　二氢黄酮及二氢黄酮醇类化合物的 ^{1}H-NMR 化学位移

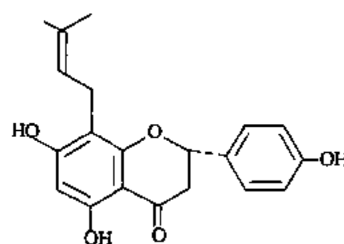
一、二氢黄酮类化合物的 ^{1}H-NMR 化学位移

表 7-10　二氢黄酮化合物 66～72 的 ^{1}H-NMR 化学位移[15,16]

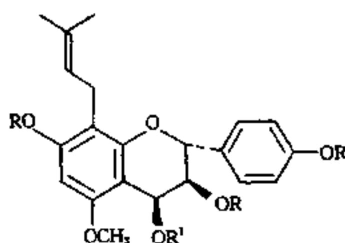
质子 \ 化合物	66	67	68	69	70	71	72
2-H	—	5.33dd	4.89d	5.26d	5.02d	5.27dd	5.41dd
3-H_α	6.64s	3.08dd	3.78ddd	5.30dd	3.85dd	3.01dd	3.02dd
3-H_β	—	2.78dd	—	—	—	2.78dd	2.87dd
4-H	—	—	4.88dd	6.44d	4.63d	—	—
6-H	6.63s	6.00s	6.18s	6.45s	6.24d	6.08s	6.11s
2′-H	7.94d	7.33d	7.35d	7.45d	7.38d	6.97d	7.53bs
3′-H	7.04d	6.88d	6.87d	7.20d	6.90d	—	—
5′-H	7.04d	6.88d	6.87d	7.20d	6.90d	6.88d	7.26d
6′-H	7.94d	7.33d	7.35d	7.45d	7.38d	6.83dd	7.35dd
1″-H	3.37bd	3.36bd	3.29bdd	3.14bd	3.30bdd	3.21bs	3.24bs
			3.20bdd		3.21bdd		
2″-H	5.30bt	5.26bt	5.20bt	5.09bd	5.25bt	5.13bt	5.13bt
4″-H	1.67bs	1.76bs	1.54bs	1.53bs	1.58bs	1.63bs	1.66bs
5″-H	1.80bs	1.82bs	1.59bs	1.62bs	1.65bs	1.64bs	1.66bs
OCH_3	—	—	3.77s	3.81s	3.85s	3.84s	3.87s
					3.56s		
OH	—	—	8.47s	—	8.42s	12.10s	12.09s
			8.33s				
			4.16d(4-HO)	—	8.33s	—	—
			3.68d(3-OH)	—	3.67s	—	—



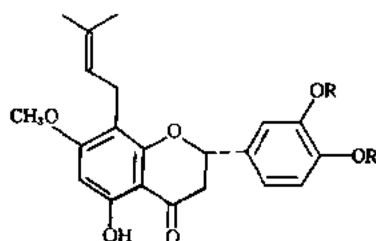
66



67



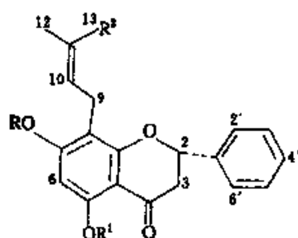
化合物 / 取代基	68	69	70
R	H	$COCH_3$	H
R^1	H	$COCH_3$	CH_3



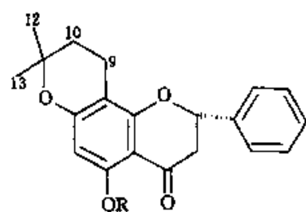
71. R = H
72. R = $COCH_3$

表 7-11　二氢黄酮化合物 73～82 的 ^{1}H-NMR 化学位移[17]

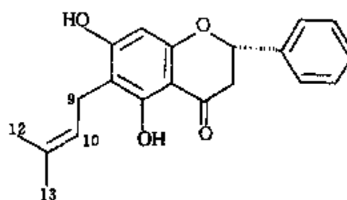
化合物 / 质子	73	74	75	76	77	78	79	80	81	82
2-H	5.43dd	5.43dd	5.49dd	5.61dd	5.48dd	5.63dd	5.48dd	5.44dd	5.46dd	5.40dd
3-H_α	3.05dd	3.12dd	3.04dd	3.14dd	3.05dd	3.19dd	3.08dd	3.04dd	2.97dd	3.08dd
3-H_β	2.84dd	2.88dd	2.79dd	2.86dd	2.80dd	2.86dd	2.82dd	2.82dd	2.73dd	2.82dd
6-H	6.04s	6.29s	6.53s	6.03s	6.55s	6.11s	6.59s	5.98s	6.18s	—
8-H	—	—	—	—	—	—	—	—	—	6.02s
9-H	3.32bd	3.22bd	3.26bd	3.36bd	3.35bd	3.63bd	3.58bd	2.61t	2.66t	3.36bd
10-H	5.22bt	5.12bt	5.09bt	5.33bt	5.38bt	6.55bt	6.38bt	1.77bt	1.78bt	5.26bt
12-H	1.72bs	1.75bs	1.66bs	1.73bs	1.71bs	1.69bs	1.66bs	1.34s	1.35s	1.82bs
13-H	1.72bs	1.69bs	1.57bs	4.18bs	4.58d	9.37s	9.36s	1.33s	1.35s	1.74bs
					4.51d					
2'～6'-H	7.45m	7.44m	7.43m	7.62m	7.44m	7.60m	7.42m	7.45m	7.44m	7.45m
				7.45m						
$COCH_3$	—	2.31s	2.32s	—	2.34s	—	2.32s	—	2.37s	—
	—	—	2.38s	—	2.37s	—	2.38s	—	—	—
	—	—	—	—	2.01s	—	—	—	—	—
OH	12.00s	12.18s	—	12.13	—	13.18s	—	11.76s	—	11.41s



化合物 / 取代基	73	74	75	76	77	78	79
R	H	$COCH_3$	$COCH_3$	H	$COCH_3$	H	$COCH_3$
R^1	H	H	$COCH_3$	H	$COCH_3$	H	$COCH_3$
R^2	CH_3	CH_3	CH_3	CH_2OH	CH_2OCOCH_3	CHO	CHO



80. R = H
81. R = $COCH_3$

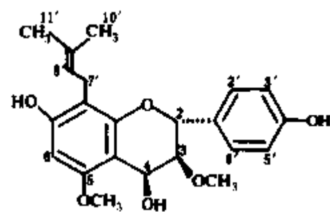


82

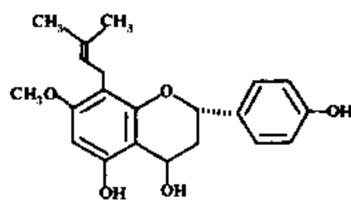
二、二氢黄酮醇类化合物的^{1}H-NMR 化学位移

表 7-12　二氢黄酮化合物 83～90 的^{1}H-NMR 化学位移[18]

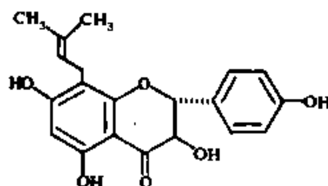
质子 \ 化合物	83	84	85	86	87	88	89	90
2-H	4.69d	5.42dd	4.62bd	4.53d	4.71d	—	—	—
3-H	4.20dd	2.57ddd	5.08bd	5.00d	4.90dd	—	—	—
		3.21dd						
4-Hα	4.49d	4.22d	—	—	4.23d	—	—	—
6-H	6.19s	5.73s	6.09s	5.96s	6.05s	5.89s	5.83s	6.30s
2′,6′-H	7.28bd	7.23bd	7.45bd	7.45bd	7.35bd	—	—	—
3′,5′-H	6.82bd	6.76bd	6.92bd	6.89bd	6.87bd	—	—	—
7′-H	3.24bd	3.13bdd	3.20bd	6.63d	6.45dd	3.35bd	2.60t	2.54t
		3.03bdd						
8′-H	5.22tqq	5.10tqq	5.18bt	5.53d	5.44d	5.26tqq	1.80t	1.80t
10′-H	1.53bs	1.64bs	1.61bs	1.45s	1.37s	1.84bs	1.37s	1.36s
11′-H	1.52bs	1.56bs	1.57bs	1.45s	1.36s	1.79bs	1.37s	1.36s
OCH_3	3.76s	3.73s	—	—	3.83s	3.84s	3.81s	3.85s
	3.36s							
OH	—	—	11.65s	11.43s	8.34s	12.80s	12.75s	2.73($COCH_3$)
	—	—	10.79s	—	—	6.27s	—	—
CHO	—	—	—	—	—	10.10s	10.07s	10.25s



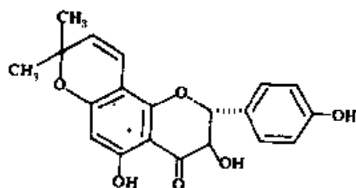
83



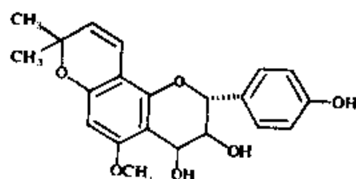
84



85



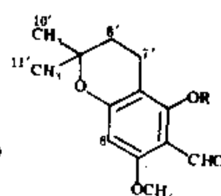
86



87



88

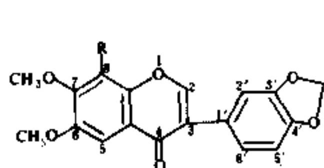


89. R = H
90. R = $COCH_3$

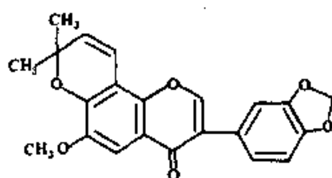
三、二氢异黄酮类化合物的¹H-NMR化学位移

表 7-13　二氢异黄酮化合物 91～97 的¹H-NMR 化学位移[19]

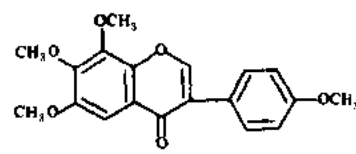
质子＼化合物	91	92	93	94	95	96	97
2-H	7.97	7.97	7.93	8.00	4.65d(7)	4.58d(7)	4.66t(7)
5-H	7.42	7.68	7.56	7.45	7.15	7.32	7.25
3-H	—	—	—	—	—	3.78t(7)	3.82t(7)
2′-H	7.07d(2)	m	7.12	—	6.74	6.75	6.80
5′-H	6.83d(8)	m	6.85d(8)	—	6.74	6.75	6.80
6′-H	6.99dd(2,8)	m	6.97	—	6.74	6.75	6.80
6-OCH_3	4.02	4.01	3.95	—	4.00	3.90	3.87
7-OCH_3	4.02	4.01	—	—	3.90	3.86	—
8-OCH_3	3.96	—	—	—	3.83	—	—
O—CH_2—O	5.96	6.02	5.97	—	5.92	5.90	5.95



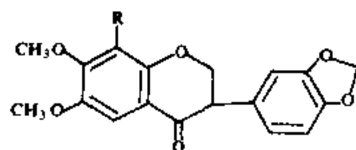
91. R = OCH_3
92. R = H



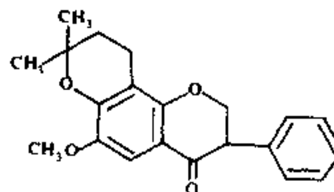
93



94



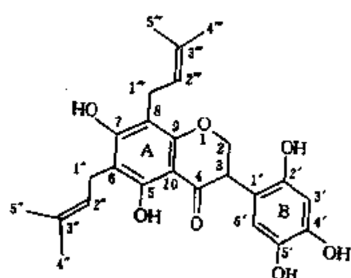
95. R = OCH_3
96. R = H



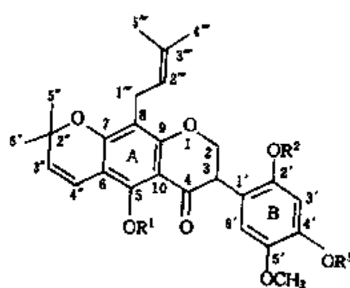
97

表 7-14　二氢异黄酮化合物 98 和 99 的¹H-NMR 化学位移[29]

质子＼化合物	98	99	质子＼化合物	98	99
1-H	—	—	5′-H	—	—
2-H	4.75dd(7.0,12.0)	4.74dd(7.0,12.0)	6′-H	7.02s	7.01s
	4.90dd(4.0,12.0)	4.91dd(4.0,12.0)	1″-H	3.20～3.25m	—
3-H	3.97t(4.0)	3.98t(4.0)	2″-H	5.15～5.22m	—
4-H	—	—	3″-H	—	5.49d(10.0)
5-H	—	—	4″-H	1.70	6.60d(10.0)
6-H	—	—	5″-H	1.80s	1.44s
7-H	—	—	6″-H	—	1.49s
8-H	—	—	1‴-H	3.20～3.25m	3.23d(7.0)
9-H	—	—	2‴-H	5.15～5.22m	5.15t(7.0)
10-H	—	—	3‴-H	—	—
1′-H	—	—	4‴-H	1.71s	1.69s
2′-H	—	—	5‴-H	1.83s	1.80s
3′-H	6.62s	6.60s	5-OH	12.18s	12.20s
4′-H	—	—	5-OCH_3	—	3.83



98

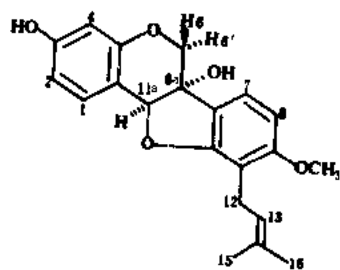


99. $R^1 = R^2 = R^3 = H$

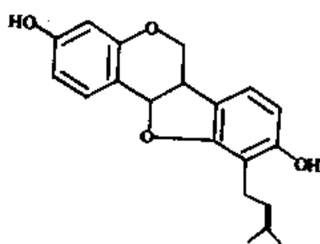
表 7-15　其他二氢异黄酮化合物 100～105 的 ^{1}H-NMR 化学位移[20]①

质子＼化合物	100	101	102	103	104	105
1-H	7.33d(8,5)	7.37d(8.5)	7.30d(8,3)	7.35d	7.18s	7.45d(8)
2-H	6.56dd (8.5,2.3)	6.53dd	6.55dd (8.3,2.5)	6.56dd	—	6.66dd (8,2.5)
4-H	6.31d(2.3)	6.40d	6.32d(2.3)	6.36d	6.40s	≈6.4
7-H	7.18d(8)	6.93d(8,5)	7.20d(8.3)	7.07d	7.20d(8.6)	7.10d(8)
8-H	6.54d(8)	6.36d(8,5)	6.42dd (8.1,2.2)	6.28d	6.42dd (8.2,2.1)	≈6.4
10-H	—	—	6.22d(2)	—	6.25d(2.1)	≈6.4
6 或 6′-H	4.06d(12) 4.16d	3.63 4.21	4.02d(11.6) 4.16d	3.63	4.01d(11.4) 4.13d	4.24
6-a-H	—	3.54	—	3.5	—	—
11-a-H	5.27s	5.44d	5.26s	5.54d	5.20s	5.52d(7)
12-H	3.25d(7)	3.36d	—	—	3.25d(7.2)	—
13-H	5.16t(7)	5.28t	—	—	5.24t(7)	—
15 或 16-H	1.65s,3.83s	1.76s,1.81s	—	—	1.72s	—
OCH_3			—	—	3.79s	3.80s

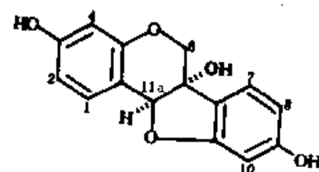
① 括号数字为 *J* 值。



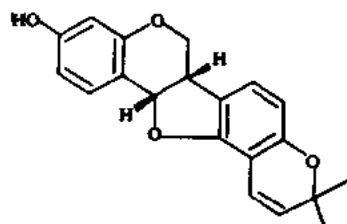
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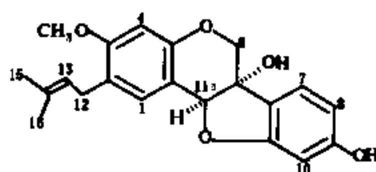
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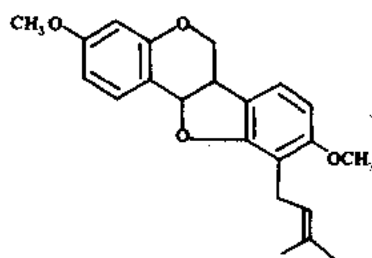
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103



104



105

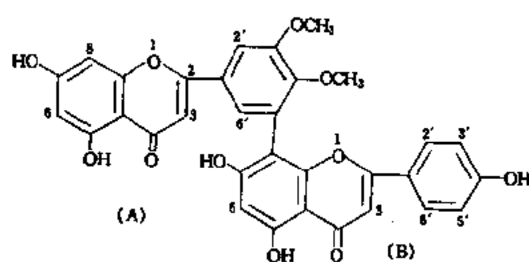
第三节　双黄酮、色酮、𠮶酮类化合物的^{1}H-NMR化学位移

一、双黄酮类化合物的^{1}H-NMR化学位移

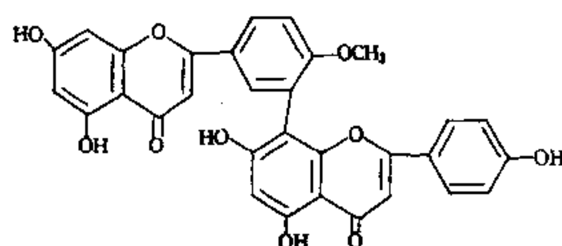
表 7-16　双黄酮化合物 106～109 的^{1}H-NMR 化学位移[21,22]①

质子＼化合物	106	107	108	109
A-3-H	7.08s	6.93s	6.60s	6.58s
A-6-H	6.22d(2)	6.21d(2)	6.05d(2)	6.04d(2)
A-8-H	6.51d(2)	6.50d(2)	6.32d(2)	6.32d(2)
A-2′-H	7.72d(2)	8.07d(2)	7.24	7.50
A-5′-H	—	7.36d(9)	7.18	7.42
A-6′-H	7.76d(2)	8.19dd(2,9)	7.24	7.50
B-3-H	6.80s	6.80s	6.60s	6.58s
B-6-H	6.42s	6.41s	6.86	6.80
B-7-H	—	—	7.70	7.80
B-2′-H	7.54d(9)	7.52d(9)	6.76	6.70
B-3′-H	6.71d(9)	6.72d(9)	—	—
B-5′-H	6.71d(9)	6.72d(9)	6.78	6.74
B-6′-H	7.54d(9)	7.52d(9)	6.96	6.92
A-5-OH	—	—	12.8～13.0br	12.8～12.96br
B-5-OH	—	—	13.1～13.30br	13.1～13.30br
OCH_3	3.63s	3.79s	3.80s	3.86(12H)
			3.84s	
	4.03s		3.86s	

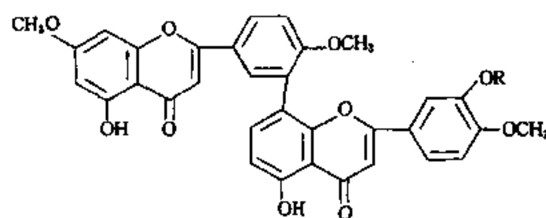
① 括号内的数字为 J 值。



106

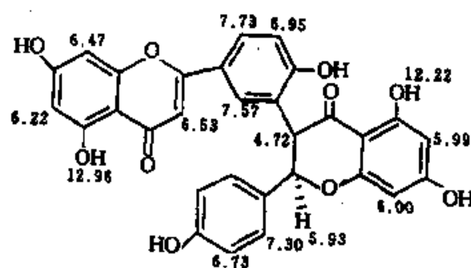


107

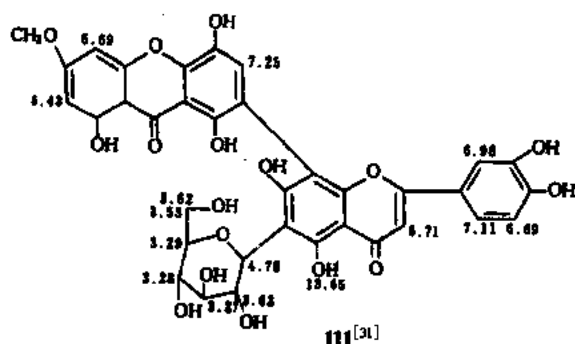


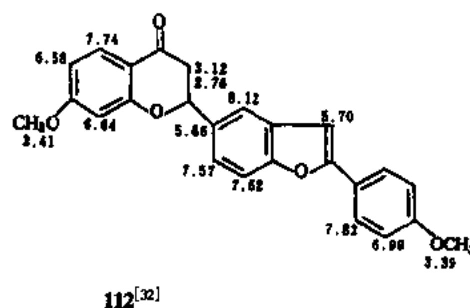
108. R＝H

109. R＝CH_3



110[30]

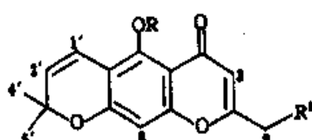

111[31]


112[32]

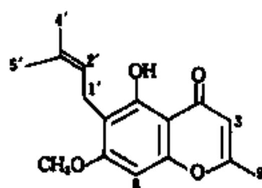
二、色酮类化合物的¹H-NMR化学位移

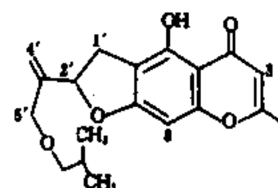
表7-17 色酮化合物113～118的¹H-NMR化学位移[18]

质子＼化合物	113	114	115	116	117	118
3-H	6.00bs	5.93q	6.19t	6.30t	6.03q	6.02bs
8-H	6.27bs	6.65d	6.29d	6.28bs	6.36s	6.31s
9-H	2.33d	2.29d	4.96bs	3.86d 3.77d	2.34bs	2.34d
1′-H	6.70bd	6.48dd	6.70dd	6.70dd	3.34bd	3.46dd 3.18dd
2′-H	5.60d	5.74d	5.62d	5.61d	5.21t	5.44dd
4′-H	1.40s	1.48s	1.47s	1.48s	1.79bs	5.36bs 5.29bs
5′-H	1.40s	1.48s	1.47s	1.48s	1.68bs	4.73bd 4.65bd
OCH_3	—	—	—	—	3.88s	—
$OCOCH_3$	—	2.45s	—	—	—	—
OCOR	—	—	2.68qq 1.25d	—	—	—
OH	13.0s	—	12.80s	12.80s	12.76s	12.92s

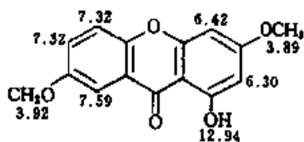


113. R = R¹ = H
114. R = $COCH_3$, R¹ = H
115. R = H, R¹ = O-异丁基
116. R = H, R¹ = OH

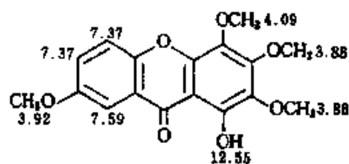

117


118

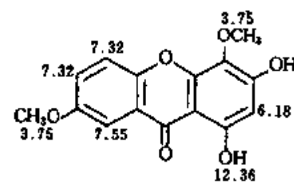
三、咄酮类化合物的^{1}H-NMR 化学位移[23~25]



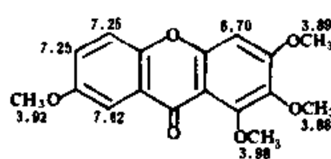
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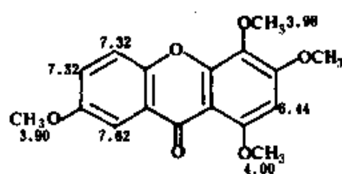
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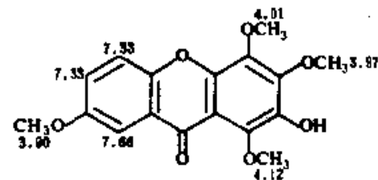
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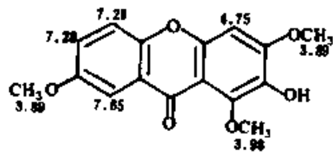
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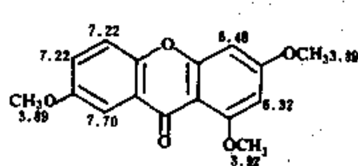
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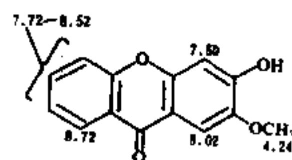
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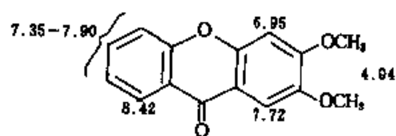
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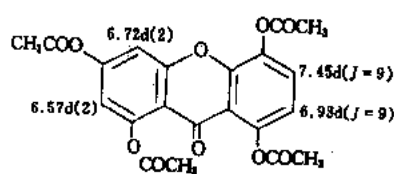
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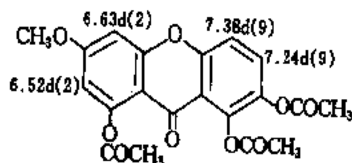
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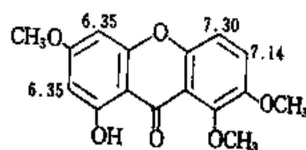
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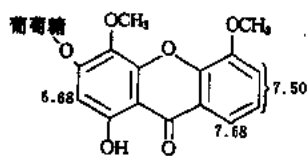
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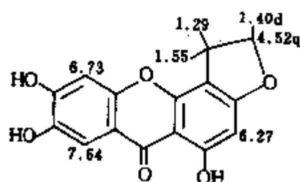
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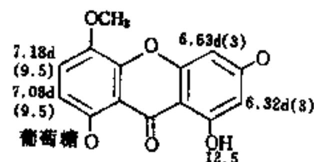
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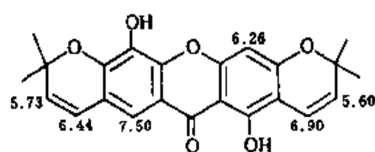
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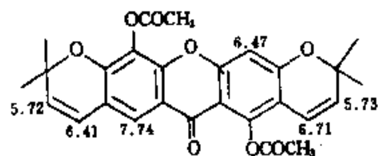


133



134





135　　　　136

第四节　黄酮类化合物的¹H-NMR 谱图

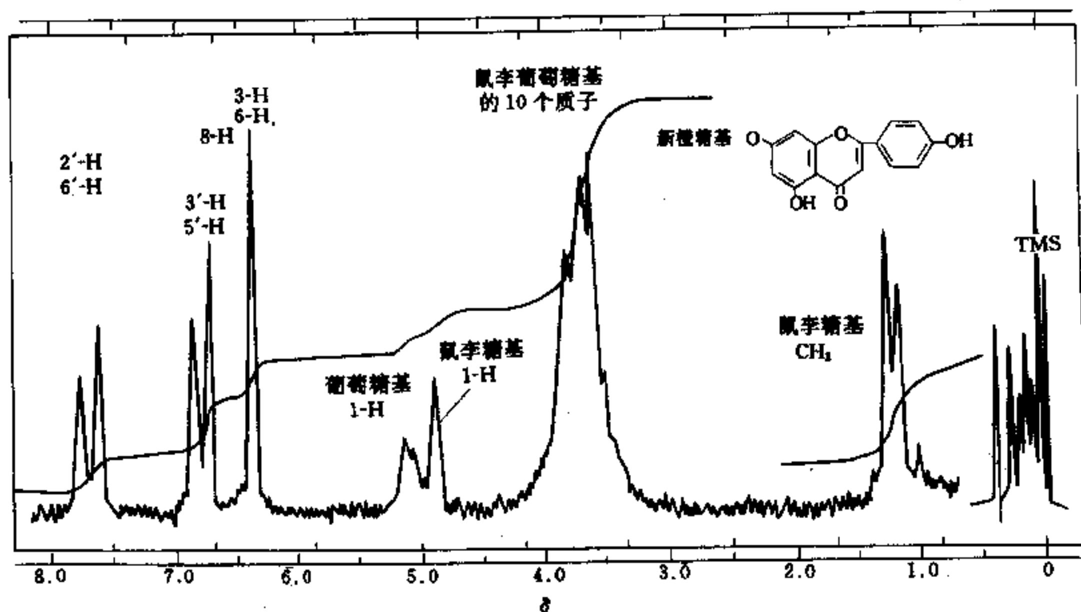


图 7-1　洋芹素-7-新橙皮糖甙三甲硅醚在四氯化碳中的核磁共振谱

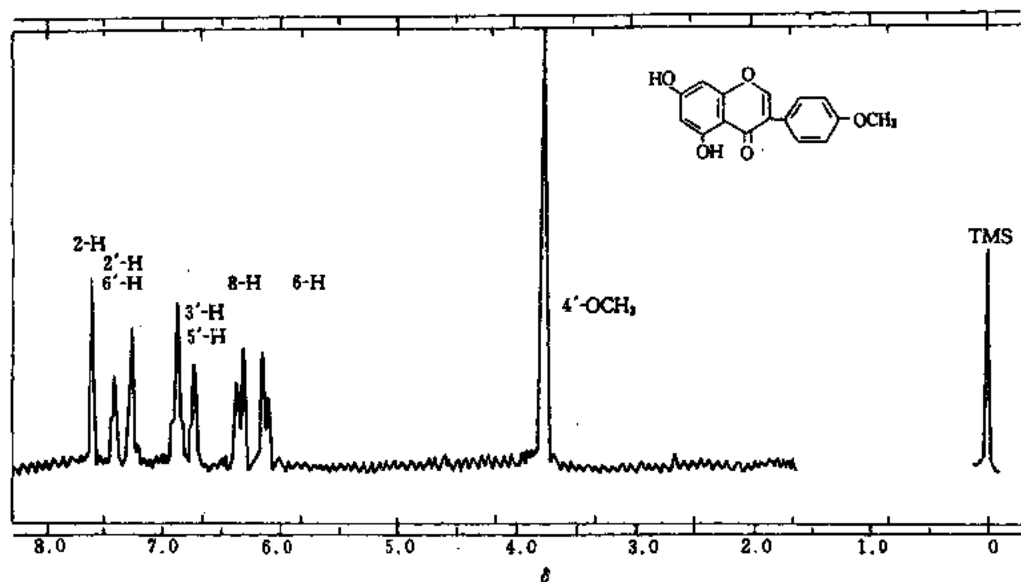


图 7-2　鹰嘴豆素甲的三甲硅醚在四氯化碳中的核磁共振谱

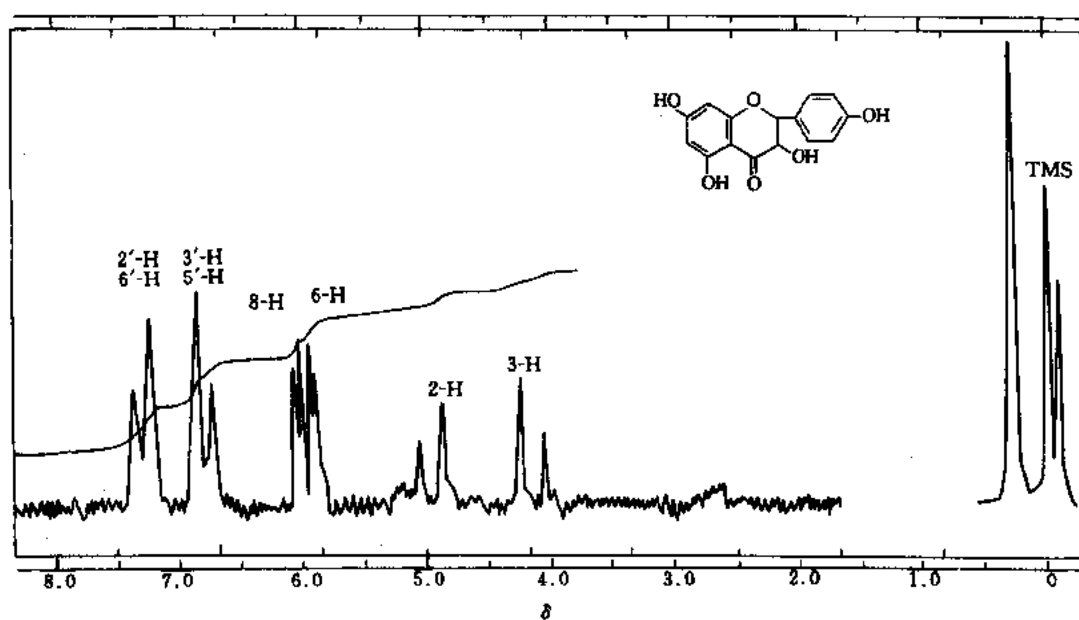


图 7-3　双氢山奈素的三甲硅醚在四氯化碳中的核磁共振谱

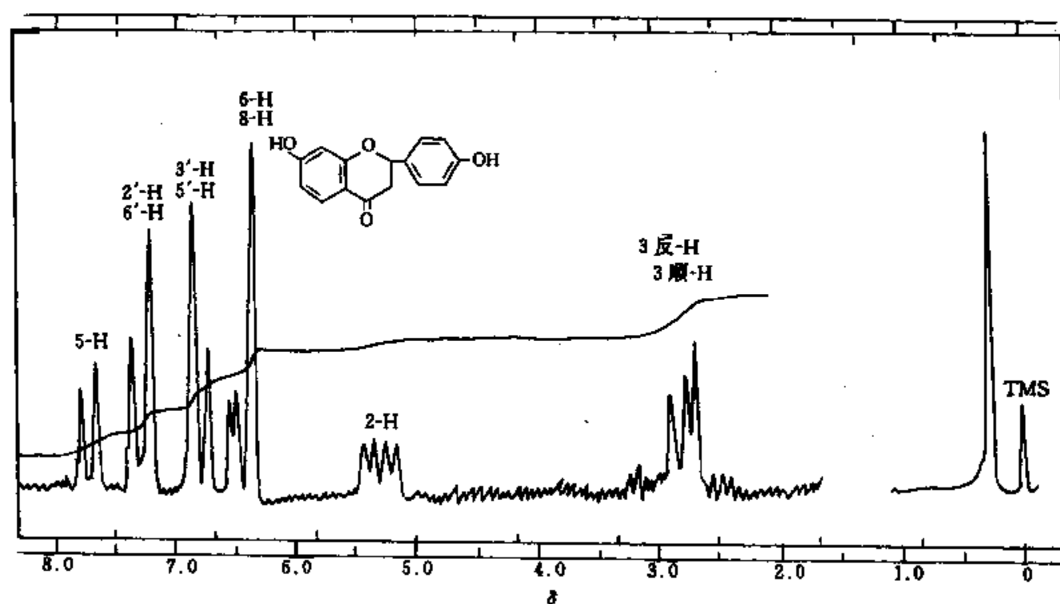


图 7-4　甘草素的三甲硅醚在四氯化碳中的核磁共振谱

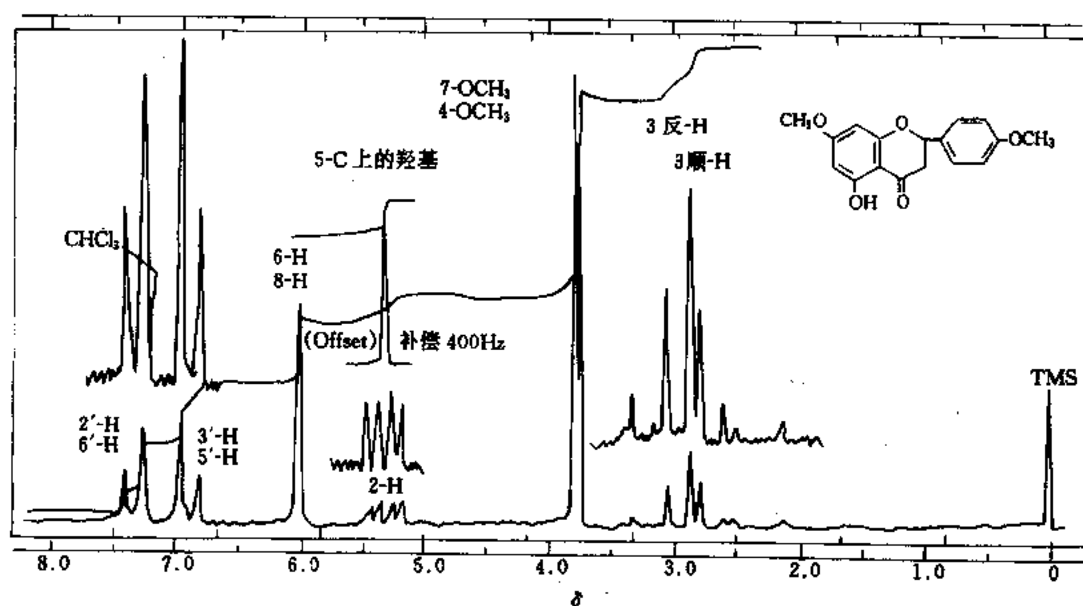


图 7-5 柚皮素-4'，7-二甲醚在氘氯仿中的核磁共振谱

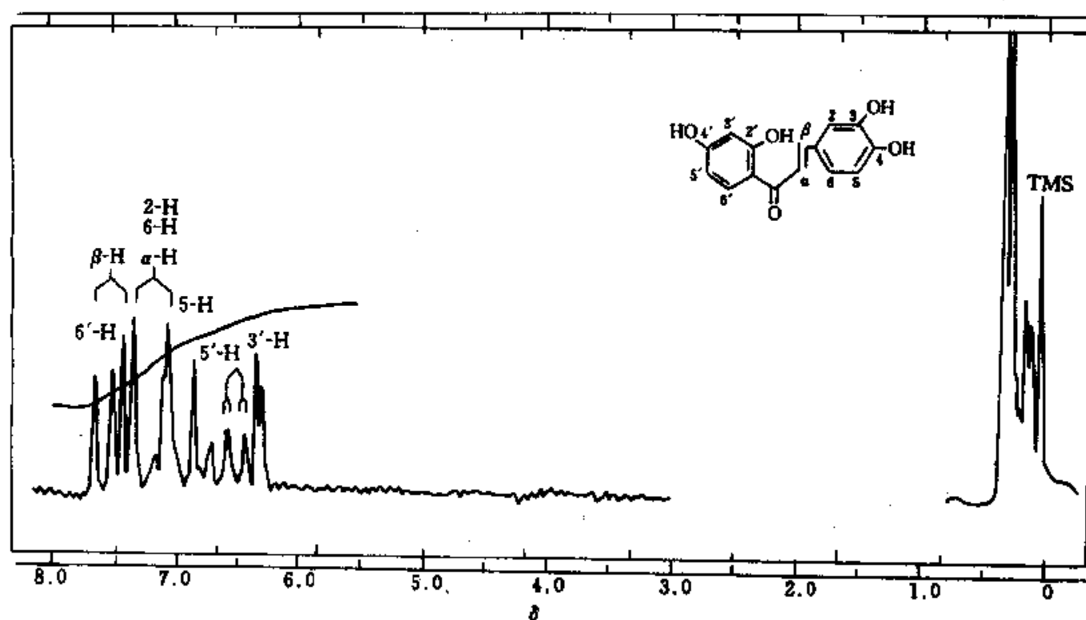


图 7-6 2',3,4,4'-四羟查尔酮的三甲硅醚在四氯化碳中的核磁共振谱

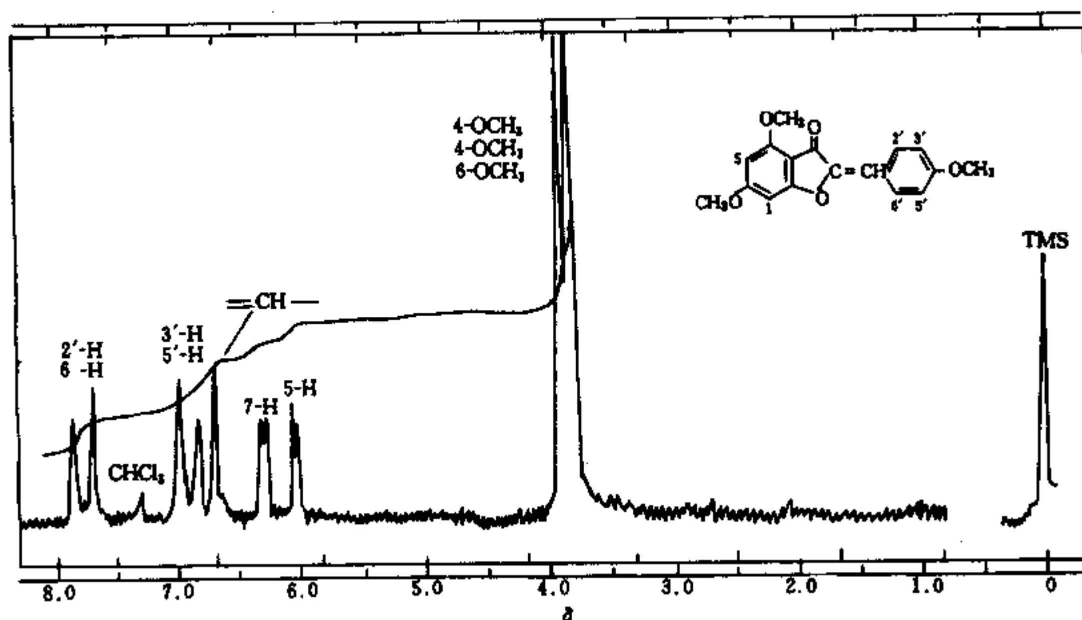


图 7-7 4,4′,6-三甲氧噢哢在氘氯仿中的核磁共振谱

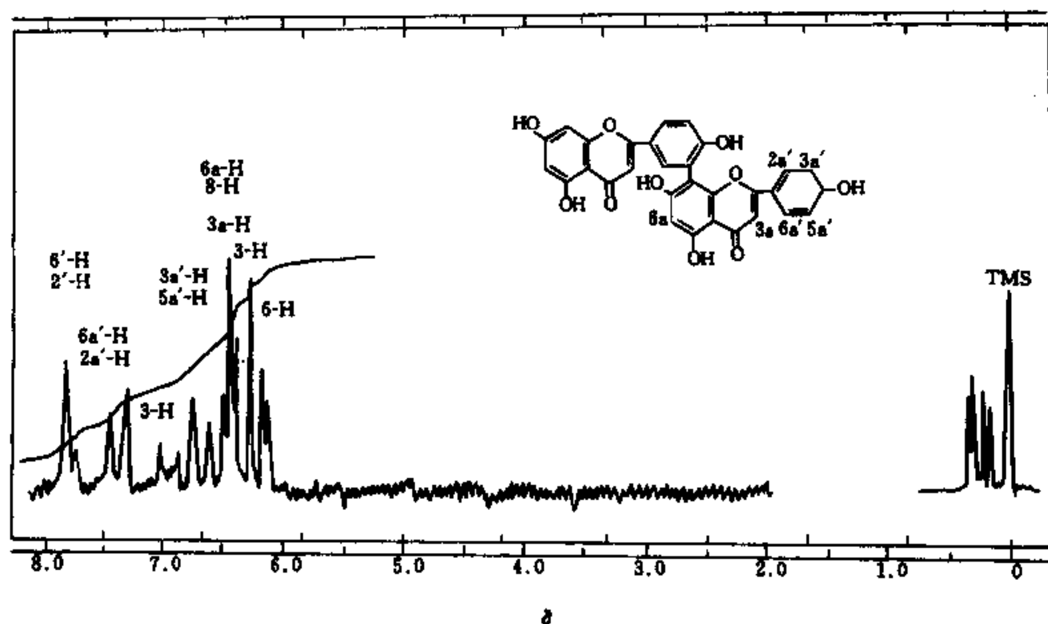


图 7-8 穗花杉双黄酮的三甲硅醚在四氯化碳中的核磁共振谱

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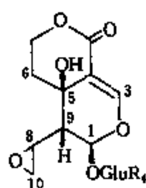
第八章　单萜及倍半萜化合物的 ^{1}H-NMR 化学位移和偶合常数

第一节　单萜类化合物的 ^{1}H-NMR 化学位移

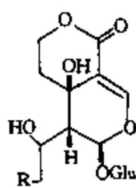
表 8-1　环烯醚萜甙类化合物 1～10 的 ^{1}H-NMR 化学位移[1]

质子 \ 化合物	1	2	3	4	5	6	7	8	9	10
1-H	5.96d(1)①	6.03d(1)	6.00d	5.75d	5.50d	5.81d	5.63d	5.45d	5.50d	5.80d
			(0.5)	(1.5)	(1.5)	(0.5)	(1.5)	(2.5)	(2.5)	(0.5)
3-H	7.73 s	7.69 s	7.70 s	7.68 s	7.50 s	7.45 s	7.49 s	5.85 s	5.87 s	7.47 s
5-OH	—	—	—	—	3.77bs	3.88bs	3.72bs	—	—	3.83bs
6-H	1.83～	1.93～	2.00～	—	—	—	—	—	约 2.67	—
	2.42 m	2.33 m	2.28 m							
8-H	2.70～	—	—	5.35～	5.30～	—	2.45～	约 4.07	—	—
	3.08 m			5.50 m	5.45 m		3.00 m			
9-H	2.70～	2.68	2.60	—	2.67～	2.80	2.45～	约 3.55	—	2.74
	3.08 m	(6,0.5)	(6,0.5)		3.30 m	(6.0,0.5)	3.00 m			(6,0.5)
10-H	2.70～	约 3.48	约 3.50	5.35～	5.30～	3.57～	2.45～	3.05～	3.46～	—
	3.08 m			5.50 m	5.45 m	3.75 m	3.00 m	(11,9)	(9,5)	
								3.51		
								(11,5)		
O—C(=O)—CH_3	—	—	—	—	2.02～	2.0～	2.01～	1.95～	1.96～	2.02～
					2.10	2.11	2.10	2.09	2.08	2.11

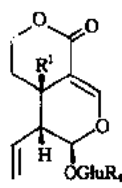
① 括号内的数字是偶合常数。



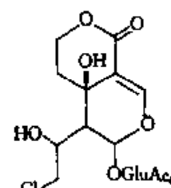
1. R = H
7. R = Ac



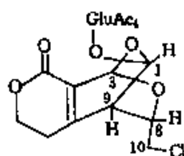
2. R = Cl
3. R = OH



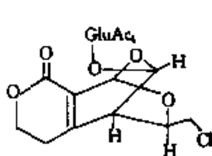
4. R = H, R^1 = OH
5. R = Ac, R^1 = OH



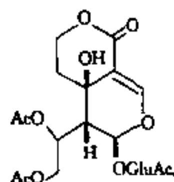
6



8



9



10

表 8-2 环烯醚萜甙类化合物 11～13 的^{1}H-NMR 化学位移[2]

质子 \ 化合物 δ	11 δ_{CDCl_3}	11 $\delta_{C_6D_6}$	12 δ_{CDCl_3}	12 $\delta_{C_6D_6}$	13 δ_{CDCl_3}	质子 \ 化合物 δ	11 δ_{CDCl_3}	11 $\delta_{C_6D_6}$	12 δ_{CDCl_3}	12 $\delta_{C_6D_6}$	13 δ_{CDCl_3}
1-H	5.84	6.14	5.84	6.14	6.20	11-H_A	4.47	4.19	4.46	4.17	4.43
3-H	6.51	6.25	6.51	6.26	6.44	11-H_B	4.65	4.43	4.68	4.54	4.56
5-H	2.96	2.85	2.96	2.86	2.95	O-A_C	2.08	1.72	2.04	1.56	2.05
6α-H	2.27	1.98	2.25	～1.9	2.10	*i*-Val(α,β)	2.17	1.92	2.19	2.08	2.21
6β-H	2.00	1.84	2.02	～1.8	2.10	*i*-Val(γ)	0.95	0.79	0.96	0.86	0.99
7-H	4.97	5.13	4.95	5.09	4.93	*i*-Val′(α,β)	2.17	2.01	2.19	2.01	2.21
9-H	2.71	2.45	2.71	2.44	2.55	*i*-Val′(γ)	0.96	0.83	0.96	0.82	0.99
10-H_A	2.81	2.40	2.81	2.36	3.51	OH	—	—	—	—	2.47
10-H_B	3.05	2.87	3.06	2.82	3.58						

11. $R^1 = R^2 = i$-Val, R^3 = Ac
12. $R^1 = i$-Val, R^2 = Ac, $R^3 = i$-Val
13. $R^1 = i$-Val, $R^2 = i$-Val, R^3 = Ac

表 8-3 环烯醚萜甙类化合物 14～16 的^{1}H-NMR 化学位移[3]

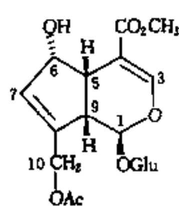
质子 \ 化合物①	14	15	16	质子 \ 化合物①	14	15	16
CO_2—CH_3	3.57 s	3.60 s	3.60 s	3-H	7.46 s	7.50 s	7.50 s
1-H	5.29d(5.4)	5.54d(5)	5.35d(4.5)	2′,6′-H	7.55d(8.5)	7.58(8)	7.20d(8.5)
7-H	5.74 m	5.78 m	5.78 m	α-H	7.57d(16)	7.76d(16)	7.62d(16)
β-H	6.35d(16)	6.47d(16)	6.45d(16)	ϕ-OH	9.96 s	—	—
3′,5′-H	6.79d(8.5)	7.40d(8)	6.83d(8.5)	ϕ-O-CH_3	—	3.81 s	3.80 s

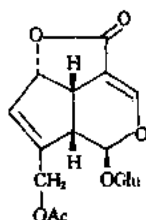
① 括号内的数字为 *J* 值。

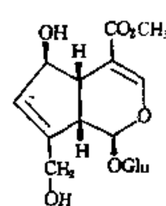
14. R = HO—C_6H_4—CH=CH—CO— (α, β; 2′, 3′, 5′, 6′)
15. R = CH_3O—C_6H_4—CH=CH—CO—
16. R = HO—$C_6H_3(CH_3)$—CH=CH—CO—

表 8-4 环烯醚萜甙类化合物 17～19 的^{1}H-NMR 化学位移[4]

质子 \ 化合物	17	18	19	质子 \ 化合物	17	18	19
1-H	4.64d	5.86d	5.15d	9-H	2.55t	—	3.00m
3-H	7.57d	7.22d	7.50s	10-H	4.74s	—	—
5-H	2.95t	—	3.00m	Ac	2.02s	2.00s	—
6-H	4.97d	5.47d	5.80s				
7-H	5.92s	5.64s	6.40s	$-C(=O)-OCH_3$	3.69s	—	3.75s



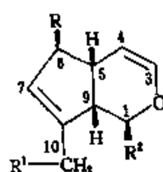




17　　18　　19

表 8-5　环烯醚萜苷类化合物 20～23 的^{1}H-NMR 化学位移[5]

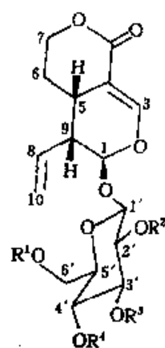
质子 \ 化合物	20	21	22	23
1-H	5.22d(5)	5.28d(5)	5.20d(5)	5.1～5.3
3-H	6.38dd(6,1.5)	6.35dd(6,1.5)	6.38dd(6,1.6)	6.20dd(6,1.5)
4-H	5.17dd(6,3.7)	5.16dd(6,3.7)	5.16dd(6,3.7)	4.9～5.0
5-H	2.9～3.2	2.84bs	2.98bs	2.84bs
6-H	4.60bs	4.60bs	4.60bs	4.40bs
7-H	5.98bs	5.89bs	5.98bs	5.90bs
9-H	2.9～3.2	3.16bt	3.10bd	3.06bs
10-H	4.38bs	4.34bs	4.36bs	4.77bs

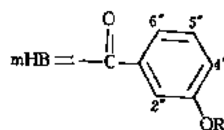


化合物 \ 取代基	R	R¹	R²
20	—O—β—D—xyl	OH	—O—β—D—glu
21	OH	OH	—O—β—D—glu
22	—O—α—L—rham	OH	—O—β—D—glu
23	—O—α—L—rham(OAc)$_3$	OAc	—O—β—D—glu(OAc)$_4$

表 8-6　环烯醚萜苷类化合物 24～29 的^{1}H-NMR 化学位移[6]

质子 \ 化合物	24	25	26	27	28	29
1-H	5.76d(2)	5.58d(2)	5.61d(2)	5.75d(2)	5.72d(2)	5.71d(2)
3-H	7.93d(2)	7.64d(2)	7.69d(2)	7.88d(2)	7.90d(2)	7.89d(2)
5-H	2.8～3.2m	2.7～3.1m	2.7～3.12m	2.82～3.20m	2.7～3.20m	2.7～3.10m
6-H	1.2～1.8m	1.1～1.5m	1.12～1.82m	1.2～1.65m	1.2～1.6m	1.17～1.77m
7-H	3.9～4.2m	4.0～4.3m	4.0～4.26m	4.0～4.30m	4.0～4.3m	3.9～4.3m
9-H	2.63bt(7)	2.55bt(7)	2.53bt(7)	2.63bt(7)	2.60bt(7)	2.6bt(7)
8-H,10-H	4.87～5.67m	4.80～5.44m	4.80～5.40m	4.86～5.30m	4.86～5.30m	4.9～5.6m
1′-H	5.30d(8)	5.52d(8)	5.46d(8)	5.37d(8)	5.34d(8)	5.28d(8)
2′-H	4.1～4.67m	5.78t(8)	5.86t(8)	4.35～4.63m	4.0～4.57m	4.02～4.4m
3′-H	4.1～4.67m	6.07t(8)	4.26～4.80m	6.10t(10)	4.0～4.57m	4.02～4.4m
4′-H	4.1～4.67m	4.36～4.65m	4.31～4.70m	4.35～4.63m	5.90t(10)	4.02～4.4m
5′-H	3.60～4.10m	3.72～4.0m	3.65～4.00m	3.62～3.98m	3.7～4.0m	3.6～4.0m
6′-H	4.1～4.67m	4.36～4.65m	4.26～4.80m	4.35～4.63m	4.0～4.57m	5.0～5.2m
2″-H	—	8.04bs	8.01bs	8.01bs	8.02bs	8.00bs
4″-H	—	7.72～7.88m	7.72～7.92m	7.67～7.85m	7.67～7.87m	7.70～7.86m
5″-H	—	7.44t(8)	7.43t(8)	7.20～7.40m	7.3～7.4m	7.23～7.43m
6″-H	—	7.37bs	7.37bs	7.20～7.40m	7.3～7.4m	7.23～7.43m

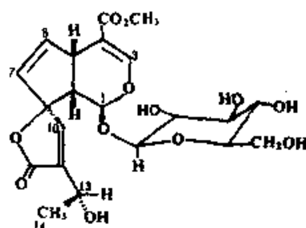




取代基 / 化合物	R¹	R²	R³	R⁴	取代基 / 化合物	R¹	R²	R³	R⁴
24	H	H	H	H	**27**	H	H	mHB	H
25	H	mHB	Ac	H	**28**	H	H	H	mHB
26	H	mHB	H	H	**29**	mHB	H	H	H

表 8-7 环烯醚萜甙类化合物 30 的¹H-NMR 化学位移[7]

质　子	δ(J)	质　子	δ(J)
1-H	5.27d(7)	9-H	3.01dd(7,5.5)
3-H	7.85s	10-H	7.57s
5-H	5.39dd(5.5,2)	13-H	4.95d(7)
6-H	6.43dd(6,2)	14-H	1.60d(7)
7-H	5.55d(6)	OCH_3	3.65s



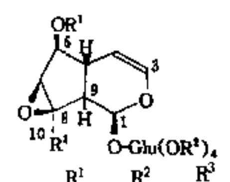
30

表 8-8 环烯醚萜甙类化合物 31～34 的¹H-NMR 化学位移[124]

化合物 / 质子	31	32	33	34
1-H	5.09(d,9.0)	5.12(d,9.3)	5.10(d,9.2)	5.02(d,9.5)
3-H	6.34(dd,1.3,7.0)	6.34(dd,1.9,6.0)	6.34(dd,1.5,6.2)	6.32(dd,1.8,6.0)
4-H	4.83(dd,3.9,7.0)	4.92(dd,4.4,6.0)	4.84(dd,4.2,6.2)	5.04(dd,4.4,6.0)
5-H	2.07(m)	2.47(ddt,1.9,4.4,7.7)	2.40(m)	2.23(ddt,1.8,4.4,7.7)
6-H	4.87(dd,1.1,6.6)	4.94(dd,1.3,7.7)	4.89(dd,1.3,7.9)	3.89(dd,1.1,7.7)
7-H	3.45(d,1.1)	3.48(br s)	3.45(d,1.1)	3.26(br s)
9-H	2.36(m)	2.41(dd,7.7,9.3)	2.40(m)	2.35(dd,7.7,9.5)
10-H	1.52(3H,s)	1.54(3H,s)	1.52(3H,s)	1.52(3H,s)
1′-H	4.76(d,7.9)	4.78(d,7.9)	4.76(d,7.9)	4.76(d,7.9)
2′-H	3.23(dd,7.9,9.5)	3.24(dd,7.9,9.0)	3.23(dd,7.9,9.2)	3.23(dd,7.9,9.4)
3′-H	3.38(t,9.5)	3.39(t,9.0)	3.38(t,9.2)	3.38(t,9.4)
4′-H	3.21(dd,8.8,9.5)	3.22(dd,9.0,9.7)	3.21(dd,8.8,9.2)	3.22(dd,8.8,9.4)

续表

质子 \ 化合物	31	32	33	34
5′-H	3.30(ddd,2.0,7.0,8.8)		3.30(ddd,2.0,6.8,8.8)	3.30(ddd,2.0,6.6,8.8)
6′-H	3.60(dd,7.0,11.9)	3.62(dd,6.8,11.9)	3.60(dd,6.8,11.9)	3.61(dd,6.6,11.7)
	3.91(dd,2.0,11.9)	3.92(dd,2.0,11.9)	3.92(dd,2.0,11.9)	3.91(dd,2.0,11.7)
3″-H	4.51(dd,3.5,11.9)	3.49(dd,4.6,10.9)	4.46(dd,3.5,11.9)	
	4.57(dd,2.0,11.9)	3.78(dd,8.8,10.9)	4.53(dd,2.6,11.9)	
4″-H	3.14(ddd,2.0,3.5,5.5)	3.03(dt,4.6,8.8)	3.12(ddd,2.6,3.5,5.9)	
5″-H	3.60(m)	3.49(m)	3.42(m)	
6″-H	2.06(m)	1.78(ddd,6.6,9.3,13.7)	1.75(ddd,9.9,12.6,19.8)	
	2.37(m)	2.28(ddd,2.8,7.5,13.7)	2.21(dddd,1.6,7.9,11.0,19.8)	
7″-H	4.52(m)	4.65(brt,6.8)	2.40(m)	
			2.58(br qui,ca,8)	
10″-H	2.18(3H,dd,0.6,2.6)	2.08(3H,brs)	2.17(3H,t,1.1)	
CH_3O—		3.76(s)		



	R^1	R^2	R^3
31.	X	H	CH_3
34.	H	H	CH_3
32.	Y	H	CH_3
33.	Z	H	CH_3

Glu = β-D-吡喃葡萄糖基

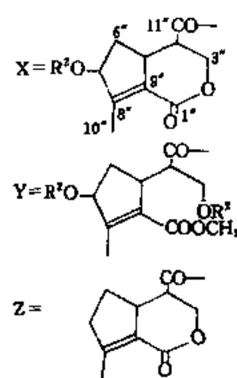
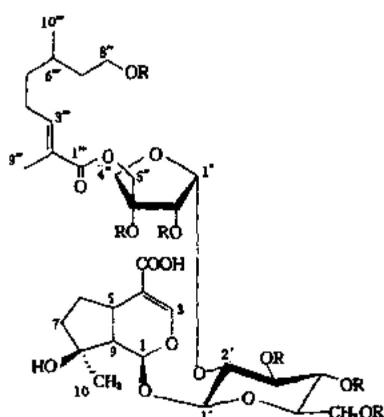


表 8-9 环烯醚萜甙类化合物 35～37 的^{1}H-NMR 化学位移[125]

质子 \ δ(J) 化合物	35		36		37	
1-H	5.39d	(5.6)	5.14d	(7.1)	5.52d	(2.8)
3-H	7.37s		7.39s		7.30s	
5-H	3.16ddd	(8.5)	3.20ddd“q”	(7.7)	3.16m	
6a-H	1.51m		1.50m		1.56m	
6b-H	2.34m		2.36m		2.31m	
7-H	1.76m		1.73t	(7.6)	1.73m	
9-H	2.14dd	(8.5,5.6)	2.12dd	(7.8,6.5)	2.27dd	(9.8,2.8)
10-H	1.39s		1.38s		1.33s	
1′-H	4.77d	(7.7)	4.86d	(7.8)	4.73d	(7.8)
2′-H	3.46dd	(9.1,7.7)	3.72dd	(9.1,7.8)	3.44dd	(9.2,7.8)
3′-H	3.55t	(8.8)	5.21t	(9.5)	3.55t	(8.6)
4′-H	3.27dd“t”	(9.7,8.3)	4.99dd“t”	(9.7,9.6)	3.28t	(9.8)
5′-H	3.35m		3.69m		3.32m	
6′a-H	3.66[b]		4.08～4.20		3.68dd	(12.0,5.8)
6′b-H	3.94brd	(12.9)	4.08～4.20		3.93dd	(12.0,2.0)
1″-H	5.41brs		5.09brs		5.43brs	
2″-H	3.92brs		5.15brs		3.93brs	
4″-H	3.79d	(9.6)	4.09d	(10.2)	4.01d	(9.9)

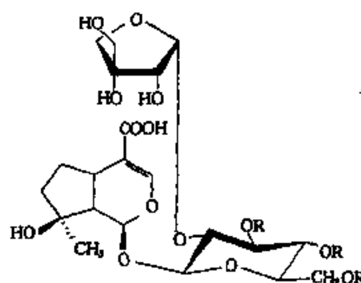
续表

δ(J) 化合物 质子	35		36		37	
4″-H	4.23d	(9.6)	4.30d	(10.2)	3.75d	(9.9)
5″-H	4.27d	(11.3)	4.73d	(12.7)	3.62brs	
5″-H	4.22d	(11.3)	4.54d	(12.7)		
3‴-H	6.86brt	(7.5)	6.75dt	(7.2,1.0)		
4‴-H	2.27m		2.20m			
5‴-H	1.36m		1.30m			
5‴-H	1.48m		1.50m			
6‴-H	1.67m		1.60m			
7‴-H	1.50m		1.50m			
7‴-H	1.62m		1.70m			
8‴-H	3.66		4.20d	(3.0)		
9‴-H	1.87s		1.81brs			
10‴-H	0.99d		0.94d	(6.0)		



35. R=H

36. R=Ac



37. R=H

第二节　倍半萜类化合物的^{1}H-NMR 化学位移和偶合常数

一、甜没药烷衍生物的^{1}H-NMR 化学位移

表 8-10　没药烷衍生物 38,39 的^{1}H-NMR 化学位移[8]

化合物 质子	38	39	化合物 质子	38	39
1-α-H	2.0m	2.0m	12-,13-H	1.26s	1.26s
1-β-H	2.18dd	2.13dd	14-H	5.27s	5.26s
2-H	3.18d	3.19d	14′-H	5.05s	5.07s
4-H	5.33bd	5.34m	15-H	1.28s	1.29s
5-H	4.97dd	5.34m	OCOR	6.11qq	6.10qq
6-H	2.57dd	2.48dd		6.08qq	1.99dq
8-H	5.49dd	5.35dd		2.00dq	
9-H	2.0m	2.0m		1.90dq,1.88dq	1.92dq,1.87dq
10-H	2.79dd	2.75dd			

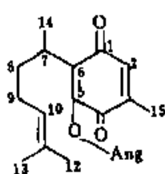
化合物 \ 取代基	R[1]	R[2]	R[3]	R[4]
38	Ang	H	Ang	H
39	H	Ang	H	Ang

表 8-11 没药烷衍生物 40,41 的[1]H-NMR 化学位移[9]

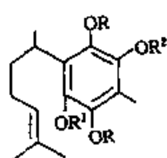
化合物	40	41

表 8-13　没药烷衍生物 45 ~ 49 的¹H-NMR 化学位移[12]

质子 \ 化合物	45	46	47	48	49
2-H	6.58q	—	—	—	—
7-H	3.02tq	3.02tq	3.08tq	2.89tq	2.87tq
10-H	5.04tqq	5.04tq	5.04tq	5.02bt	5.04bt
12-H	1.53bs	1.52bs	1.54bs	1.53bs	1.55bs
13-H	1.64bs	1.63bs	1.64bs	1.64bs	1.67bs
14-H	1.20d	1.21d	1.21d	1.20d	1.21d
15-H	2.05bs	1.96s	1.94s	1.98s	1.97s
OCOR	6.34bq	6.34bq	6.34bq	6.31qq	6.30qq
	2.05m	2.06bd	2.06bd	2.07dq	2.07dq
	—	2.03bs	2.03bs	2.04bs	2.03dq
OAc	—	—	—	2.29s	2.29s
				3.28s	2.28s
				2.22s	2.23s



45

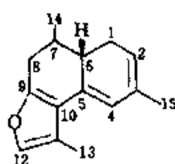


取代基 \ 化合物	46	47	48	49
R	H	H	Ac	Ac
R¹	H	Ang	Ac	Ang
R²	Ang	H	Ang	Ac

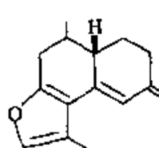
二、荜橙茄烷衍生物的¹H-NMR 化学位移和偶合常数

表 8-14　荜橙茄烷衍生物 50 ~ 52 的¹H-NMR 化学位移[10]

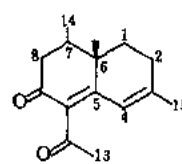
质子 \ 化合物	50	51	52	质子 \ 化合物	50	51	52
1-H	2.3 ~ 2.5m	—	1.35m	7-α-H	—	—	1.88m
2-H	5.48m	2.35 ~ 2.55m	2.25m	12-H	7.03bs	7.03bs	—
4-H	6.02bs	6.42bs	6.15bs	13-H	2.18bs	2.19bs	2.36s
6-β-H	—	—	2.04m	14-H	1.11d	1.12d	1.11d
8-α-H	2.76dd	2.75dd	2.50dd	15-H	1.80bs	4.81bs	1.91bs
8-β-H	2.44dd	2.48dd	2.20dd	15′-H	—	4.74bs	—



50



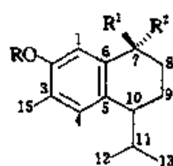
51



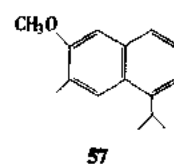
52

表 8-15 苹橙茄烷衍生物 53 ~ 58 的^{1}H-NMR 化学位移[11]

质子 \ 化合物	53	54	55	56	57	58
1-H	6.65s	6.98s	6.88s	6.89s	7.09s	7.45s
4-H	7.02bs	6.52bs	7.07bs	7.11bs	7.85bs	7.04bs
7-H	3.76dd	2.68m	3.02dddd	3.75dd	7.55bs	—
8-α-H	2.30m	1.92m	2.00m	2.28m	7.35dd	2.76dt
8-β-H	—	1.57m	1.6 ~ 1.9m	1.6 ~ 1.9m	7.35dd	2.54dt
9-α-H	1.6 ~ 1.9m	1.78m	1.6 ~ 1.9m	1.6 ~ 1.9m	7.25bd	2.00m
9-β-H	—	1.57m	1.6 ~ 1.9m	1.6 ~ 1.9m	7.25bd	2.13m
10-α-H	2.59ddd	2.62ddd	2.60ddd	2.60ddd	—	2.55ddd
11-H	2.30m	2.22dqq	2.18m	2.28m	3.70qq	2.00m
12-H	1.00d	1.02d	1.00d	1.01d	1.38d	0.98d
13-H	0.74d	0.74d	0.77d	0.75d	—	0.98d
14-H	—	—	4.28dd 4.11dd	—	—	—
15-H	2.18bs	2.18bs	2.12bs	2.13bs	2.41bs	2.31bs
OCH_3	3.76s	3.79s	—	—	3.94s	—
OAc	—	—	2.30 2.07	2.29s	—	—



取代基 \ 化合物	53	54	55	56	58
R	Me	Me	Ac	Ac	Me
R¹	H	H	H	H	} = O
R²	CO_2H	H	CH_2OAc	CO_2H	



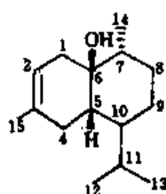
57

表 8-16 苹橙茄烷衍生物 59 ~ 64 的^{1}H-NMR 化学位移[11]

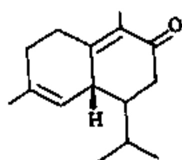
质子 \ 化合物	59	60	61	62	63	64
1-α-H	1.9 ~ 2.2m	2.87dddd	2.86bd	3.09dd	2.91bd	1.75 ~ 1.95m
1-β-H	1.9 ~ 2.2m	2.16m	3.56d	2.0m	—	1.75 ~ 1.95m
2-H	5.45bd	2.16m	—	4.08bs	3.95bs	2.3m
4-H	1.9 ~ 2.2m	5.49bs	6.67dq	5.45bs	5.47bs	5.43bs
5-H	1.9 ~ 2.2m	2.93m	3.03m	2.68m	2.60m	2.60m
8-α-H	—	—	—	2.03dd	2.40bdd	} 5.48dq
8-β-H	—	—	2.37bd	2.35bdd	5.14ddd	
9-α-H	1.6m	2.41dd	—	—	—	—
9-β-H	1.6m	2.16m	5.19ddd	5.06ddd	—	5.32ddq
10-α-H	1.6m	2.16m	—	1.50ddd	—	2.1m
11-H	1.97m	2.16m	1.8m	1.8m	—	2.1m
12-H	0.90d	0.95d	1.11d	1.06d	1.07d	0.99d
13-H	0.83d	0.86d	1.02d	0.93d	0.94d	0.90d
14-H	0.99d	1.81dd	1.65bs	1.66bs	1.73bd	1.75bs
15-H	1.72bs	1.74bs	1.75bs	1.75bs	1.77bd	1.81bs
O-Ang	— — —	— — —	6.05qq 1.96dq 1.81dq	6.02qq 1.98dq 1.86dq	6.03qq 1.98bq 1.85dq	6.06qq 1.99dq 1.87dq

表 8-17 荜橙茄烷衍生物 60,61 的偶合常数[11]

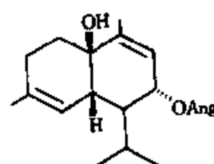
质子 \ 化合物	60	61	质子 \ 化合物	60	61
1α,1β	13.5	16.5	9β,10α	13	—
1α,2β	3	—	11,12	7	—
1α,2α	3	—	11,13	7	—
1α,14	1.5	—	4,5	—	1.5
1β,14	1	—	4,7	—	1.5
5,10	10	—	8α,8β	—	16
9α,9β	15.5	—	8α,9β	—	4
9α,10α	3.5	—	8β,9β	—	9
8β,9β	—	9	11,12	—	7
9β,10α	—	8	11,13	—	7



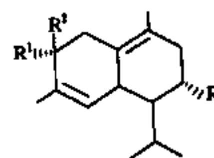
59



60



64



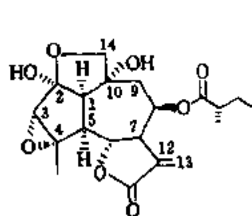
	61	62	63
R	OAng	OAng	OAng
R¹	}=0	OH	H
R²		H	OH

三、愈创木烷衍生物类化合物的¹H-NMR 化学位移

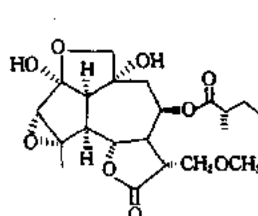
表 8-18 愈创木烷衍生物 65~70 的¹H-NMR 化学位移[13]

质子 \ 化合物①	65	66	67	68	69	70
1-H	2.63d(10)	2.59d(10)	3.35d(8)	2.13dd(4.5,7.8)	2.12dd(4.5,7)	1.75dd(4.5,7.5)
2-H	—	—	—	4.35bd(4.5)	4.31bd(4.5)	4.45bd(4.5)
3-H	3.50	3.44	3.27	3.26	3.21	3.27
5-H	2.90dd(10)	2.70t(12)	3.03dd(10,8)	2.52dd(10,7)	2.46dd(12,8)	2.26dd(11,7)
6-H	4.49dd(12,9)	4.40dd(12,9)	4.20dd(10,6)	4.73dd(10,9)	4.61dd(12,9)	4.78dd(11,9)
7-H	3.06m	2.77m	4.09m	3.97m	3.4m	3.09m
8-H	5.69m	5.35m	5.58m	5.55dt(4,8)	5.23dt(4,9)	5.39dt(4,8)
9-H	2.33m	2.39m	2.39m	2.40m	1.90m	2.93dd(14,5)
		2.32m		1.60m	2.36m	
13-H	6.32d(3.5)	3.72dd(11,3)	6.28d(3.5)	6.25d(5)	3.62dd(10,4)	6.26d(3)
	5.55d(3)	3.36dd(11,2)		5.41d(3)	3.55dd(10,3)	5.46d(3)
14-H	4.32d(12)	4.35d(10)	4.31	1.41	1.38	2.59
	4.10d(12)	4.09d(10)				
15-H	1.64	1.58	1.79	1.68	1.62	1.60

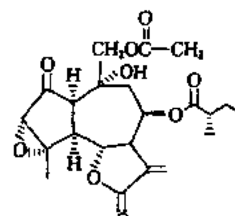
① 括号内的数字为 J 值。



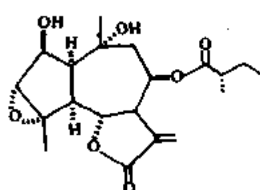
65



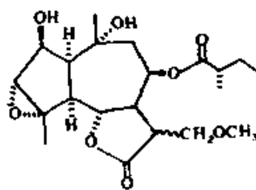
66



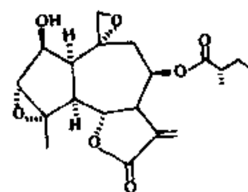
67



68



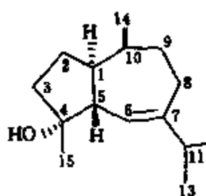
69



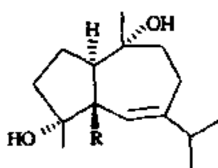
70

表 8-19 愈创木烷衍生物 71 ~ 75 的^{1}H-NMR 化学位移[14]

质子＼化合物	71	72	73	74	75	质子＼化合物	71	72	73	74	75
1-H	2.25m	—	2.68m	—	0.61bt	12-H	1.02d	0.99d	0.99d	0.98d	0.94d
5-H	2.34bd	2.18m	2.61m	2.34bd	1.84m	13-H	1.01d	0.98d	0.98d	0.97d	0.92d
6-H	5.70d	5.51d	5.15d	5.51d	5.71bd	14-H_A	4.88bs	1.28s	1.18s	0.89s	1.16s
8-αH	2.55bdd	1.94bdd	2.34bdd	2.61m	—	14-H_B	4.82bs				
11-H	2.24qq	2.24qq	2.25qq	—	2.10qq	15-H	1.15s	1.22s	1.41s	1.20s	1.20s

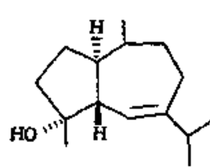


71

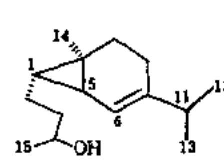


72. R = β-H

73. R = α-H



74



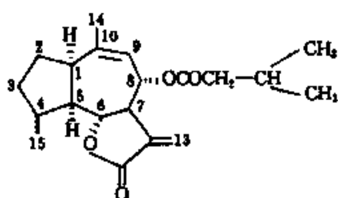
75

表 8-20 愈创木烷衍生物 76 ~ 82 的^{1}H-NMR 化学位移[15]

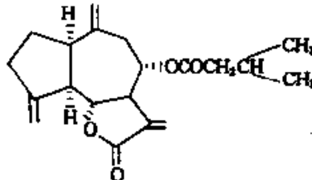
质子＼化合物	76	77	78	79	80	81	82
1-H	2.93ddd	2.92ddd	2.61ddd	2.60ddd	3.03m	2.88m	2.89m
2-H_A	2.08m	2.2m	2.26dd	2.25dd	2.06m	2.00m	2.49m
2-H_B	1.76m	—	2.11dd	2.10dd	1.9m	1.85m	1.76m
3-H	2.48m	2.51m	5.52bs	5.52bs	3.38bs	2.49bt	5.60dd
5-H	2.84dd	2.82dd	2.79dd	2.79dd	1.78dd	2.88m	2.89m
6-H	4.02dd	4.02dd	4.04dd	4.04dd	4.12dd	2.24dd(α)	2.89m
						2.00m(β)	2.22d
7-H	3.23dddd	3.14dddd	3.96dddd	3.96dddd	3.24dddd	2.80dddd	2.72dddd
8-H	5.40m	5.00ddd	5.23dd	5.23dd	5.09ddd	3.78ddd	3.78ddd
9-H	5.40m	2.17dd	2.36dd	2.36dd	2.40m	3.02dd	3.05dd
		2.27m	1.91dd	1.93dd		2.33dd	2.33dd
13-H_A	6.26bd	6.24d	6.18d	6.16d	6.24d	6.21d	6.22d

续表

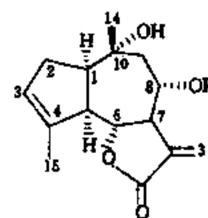
质子 \ 化合物	76	77	78	79	80	81	82
13-H_B	5.69bd	5.65d	5.50d	5.49d	5.62d	5.52d	5.51d
14-H_A	1.83bs	5.06bs	1.25s	1.24s	5.11d	5.03bs	5.09bs
14-H_B		4.94bs			4.84d	4.91bs	5.05bs
15-H_A	5.2ddd	5.30bs	1.92bs	1.93bs	1.62s	4.95ddd	5.14dd
15-H_B	5.05ddd	5.10bs				4.81ddd	5.02dd
OCOR	2.27m	2.27m	6.20bs	6.95bq	6.20bs	—	2.27bd
	2.17m	2.17m	5.70dq	1.85bd	5.69bs	—	2.13m
	1.00d	1.02d	2.01bs	1.81bs	2.00bs	—	0.99d



76

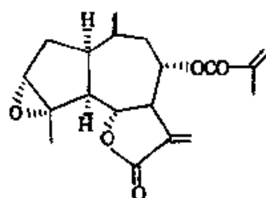


77

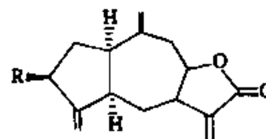


78. R = CO

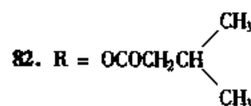
79. R = CO



80



81. R = H

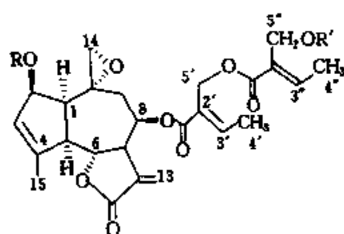


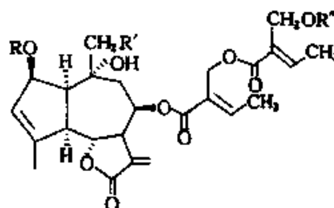
82. R = OCOCH₂CH(CH₃)₂

表 8-21 愈创木烷衍生物 83～87 的 ^{1}H-NMR 化学位移[16]

质子 \ 化合物	83	84	85	86	87
1-H	2.0	1.63dd	1.61	2.42	2.36dd
2-H	4.62ddq	5.44	5.44	5.46	4.52
3-H	5.70dq	5.48	5.50	5.76	5.75
5-H	2.76dd	2.18	2.22	2.75	2.76
6-H	4.64dd	4.61	4.61	4.50	4.57
7-H	3.56dddd	3.38	3.40	3.90	3.95
8-H	5.62ddd	5.72	5.76	5.70	5.71
9-H_A	2.65dd	2.33	2.37	2.42	2.40
9-H_B	2.22dd	2.05	2.06	2.42	2.40
13-H_A	6.29d	6.25	6.24	6.25	6.24
13-H_B	5.56d	5.20	5.24	5.47	5.46

质子 \ 化合物	83	84	85	86	87
14-H	2.57	2.22	2.25	3.65d	4.38
				3.90d	
15-H	1.99dd	1.84	1.87	2.02dq	2.02
3′-H	7.10q	6.94	6.94	7.14	7.12
4′-H	1.95	1.39	1.40	1.95	1.96
5′-H	4.89d	4.87	4.90	4.93	4.90
	4.80d	4.65	4.70	4.76	4.80
3″-H	6.91q	6.83	6.99	6.91	6.91
4″-H	1.90d	1.50	1.58	1.90	1.91
5″-H	4.30	4.31	4.89	4.30	4.31





83. R = R' = H

84. R = COCH₃, R' = H

85. R = R' = COCH₃

86. R = R" = H, R' = Cl

87. R = R" = H,

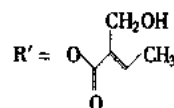
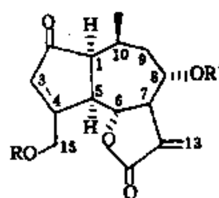


表 8-22　愈创木烷衍生物 88～91 的 ¹H-NMR 化学位移[17]

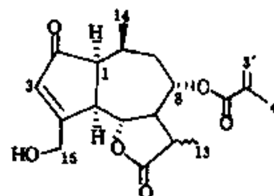
质子 \ 化合物	88	89	90	91	质子 \ 化合物	88	89	90	91
1-H	2.85m	2.86dd	2.83m	2.83m	13-H_B	5.89d	5.87d	5.82d	—
3-H	6.42t	6.23t	6.42t	6.42t	14-H	1.02d	1.03d	1.00d	0.92
5-H	3.34dd	3.34dd	3.32dd	3.32dd	15-H_A	4.62bd	5.03bd	4.62bd	4.62bd
6-H	4.42dd	4.43dd	4.40dd	4.46dd	15-H_B	4.80bd	5.22bd	4.80bd	4.80bd
7-H	3.21dddd	3.21dddd	3.22dddd	2.60m	3'-H_A	—	—	6.17bs	6.14bs
8-H	5.32ddd	5.32ddd	5.25ddd	5.25dddd	3'-H_B	—	—	5.71bs	5.67bs
10-H	2.68m	2.65m	2.67m	2.67m	4'-H	—	—	1.99bs	1.97bs
13-H_A	6.34d	6.34d	6.33d	1.33d					



88. R = H，R' = 肉桂酰

89. R = COCH₃，R' = 肉桂酰

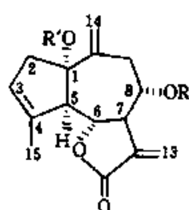
90. R = H，R' = —CO—<



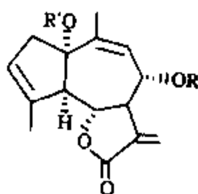
91

表 8-23　愈创木烷衍生物 92～97 的 ¹H-NMR 化学位移[18]

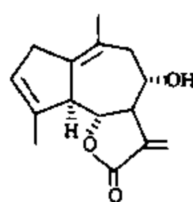
质子 \ 化合物	92	93	94	95	96	97
2-H	2.75bs	2.78bs	2.84bs	2.5～2.7m	2.5～2.7m	2.84bs
3-H	5.50bs	5.53bs	5.53bs	5.43bs	5.45bs	5.43bs
5-H	2.91bs	2.89bd	2.96bd	3.26bd	3.28bd	3.10bd
6-H	3.93dd	3.99dd	3.97dd	3.91dd	3.99dd	3.35dd
7-H	3.03m	3.30m	3.30m	3.23m	3.30m	2.53m
8-H	3.84m	4.89ddd	4.86ddd	4.16bd	5.36bd	3.42ddd
			2.73dd			2.25bdd
9-H	2.60m	2.60bd	2.64dd	5.73bd	5.65bd	1.85bdd
13-H_A	6.32d	6.31d	6.72d	6.29d	6.27d	6.14dd
13-H_B	6.20d	5.72d	5.74d	6.26d	5.74d	6.02dd
14-H_A	5.24bs	5.33bs	5.38bs	1.84bs	1.86bs	1.57dd
14-H_B	5.24bs	5.25bs	5.27bs	—	—	—
15-H	1.90bs	1.93bs	1.87bs	1.90bs	1.91bs	1.94ddd



92 ~ 94



95,96



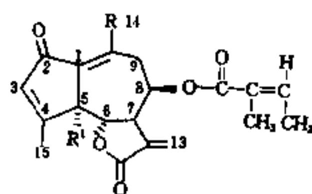
97

取代基 \ 化合物	92	93	94
R	H	$COCH_3$	$COCH_3$
R′	H	H	$COCH_3$

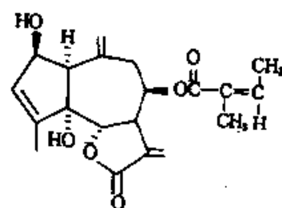
取代基 \ 化合物	95	96
R	H	$COCH_3$
R′	H	H

表 8-24　愈创木烷衍生物 98 ~ 101 的^{1}H-NMR 化学位移[19]

质子 \ 化合物	98	99	100	101	质子 \ 化合物	98	99	100	101
1-H	—	—	—	2.98d	13-H_A	6.26d	6.22d	6.25d	6.34d
2-H	—	—	—	4.85bd	13-H_B	5.58d	5.52d	5.61d	5.59d
3-H	6.29dq	6.24q	6.37dq	5.80d	14-H_A	4.54dd	4.61bd	10.92s	5.16bs
5-H	3.60bd	—	—	—	14-H_B	4.42dd	4.19bd	—	5.13bs
6-H	4.14dd	4.30d	4.43d	4.80d	15-H	2.41bs	2.37bd	2.43d	1.79bs
7-H	3.17bd	4.00bd	4.05bd	3.73dddd	OCOR	6.73qq	6.68qq	6.60qq	6.06qq
8-H	5.78bd	5.71bd	5.86bd	5.55ddd		1.77bd	1.75bd	1.72bd	1.93bd
9-H_A	3.17bd	2.96dd	3.66dd	2.94dd		1.75bs	1.71bs	1.68bd	1.95bs
9-H_B	2.71bd	3.12bd	2.64bd	2.84dd					



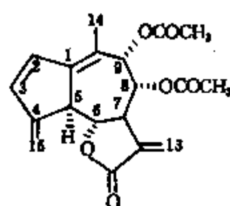
98. R = CH_2OH, R′ = H
99. R = CH_2OH, R′ = OH
100. R = CHO, R′ = OH



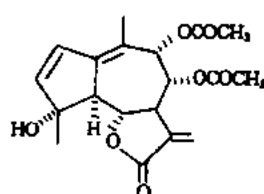
101

表 8-25　愈创木烷衍生物 102 ~ 104 的^{1}H-NMR 化学位移[20]

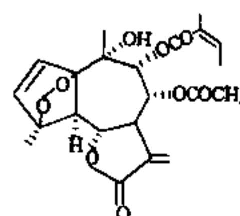
质子 \ 化合物	102	103	104	质子 \ 化合物	102	103	104
2-H	6.16bd	6.12bd	6.46d	13-H_A	6.11d	6.29d	6.20d
3-H	6.09bd	6.32bd	6.39d	13-H_B	5.31d	5.75d	5.48d
5-H	3.70dq	3.22dq	2.82d	14-H	1.80bs	1.95d	1.74s
6-H	3.01dd	4.10dd	3.94dd	15-H	5.18bs	1.50s	1.33s
7-H	3.51dddd	3.70dddd	3.74dddd		5.46bs		
8-H	4.89dd	5.19dd	5.65dd	OCOR	2.15s	2.13s	—
9-H	5.54d	5.58d	5.17d		2.14s	2.12s	—



102



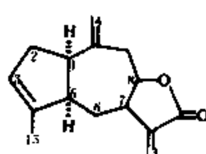
103



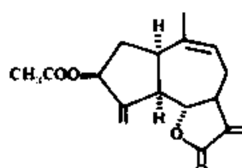
104

表 8-26 愈创木烷衍生物 105～108 的 ^{1}H-NMR 化学位移[21]

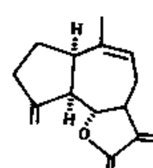
质子 \ 化合物	105	106	107	108	质子 \ 化合物	105	106	107	108
1α-H	3.15bddd	2.95ddd	2.65m	3.24ddd	8α-H	4.55ddd	—	2.02bdd	1.69ddd
2α-H	2.21dddq	—	1.57dddd	1.88m	8β-H	—	—	2.55m	2.40ddd
2β-H	2.38dddq	—	2.18dddd	2.02m	9-H	2.65bd	2.2～2.5m	5.54ddq	5.56dd
3α-H	5.35bs	5.62dddd	2.39dddd	2.15bdd	13-H_A	6.23d	6.23d	6.19d	6.25d
3β-H	—	—	2.55m		13-H_B	5.63d	5.51d	5.47d	5.49d
5α-H	2.44bddd	2.3m	2.65m	2.95bdd	14-H_A	5.00ddd	4.97bs	1.84ddd	5.18bs
6α-H	1.49ddd	—	—	—	14-H_B	4.93ddd	4.95bs	—	4.97bs
6β-H	1.67ddd	4.08dd	3.94dd	3.94dd	15-H_A	1.70m	5.48s	5.21bs	5.28bs
7α-H	3.03dddd	2.87dddd	2.70dddd	3.13dddd	15-H_B	—	5.31bs	5.04bs	5.10bs



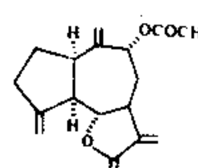
105



106



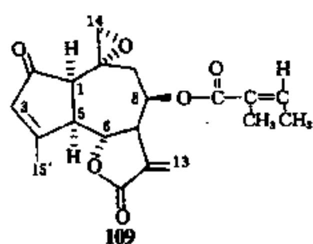
107



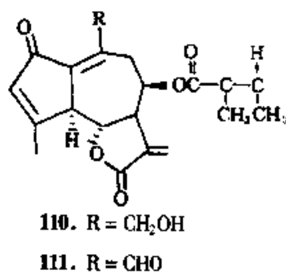
108

表 8-27 愈创木烷衍生物 109～114 的 ^{1}H-NMR 化学位移[22,23,24]

质子 \ 化合物	109	110	111	112	113	114
1-H	2.2m	—	—	—	2.82m	2.97ddd
2-H	—	—	—	1.38～2.84m	1.3～2.0m	2.61dd
						2.48dd
3-H	6.03dq	6.29dq	6.37dq	2.04m	2.20m	—
4-H	—	—	—	2.42m	—	2.22m
5-H	2.29bdd	3.60bd	3.80bd	—	—	2.30m
						3.95dd
6-H	5.12dd	4.14dd	4.20dd	2.95d	2.78d	—
				3.17d	3.23d	
7-H	2.20ddd	3.17bd	3.24ddd	—	—	2.05dddd
8-H	5.70ddd	5.78bd	5.89bd	—	—	2.54m
						1.35ddd
9-H	2.30ddd	3.17dd	3.85dd	2.77d	2.30m	4.23ddd
	1.98dd	2.71bd	2.23d			
10-H	—	—	—	2.68m	2.42m	—
11-H	—	—	—	—	—	2.30m
12-H	—	—	—	1.85s	1.76s	—
13-H_A	6.38d	6.26d	6.28d	2.04s	1.78s	1.25d
13-H_B	5.66d	5.58d	5.65d	—	—	—
14-H_A	2.10	4.54dd	11.10s	1.08d	0.90d	5.44d
14-H_B	2.10	4.42dd	—	—	—	4.83bs
15-H	2.37bs	2.41bs	2.46bs	1.07d	1.62s	1.30d
OH	—	—	4.03bd	—	—	1.81d

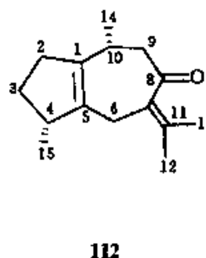


109

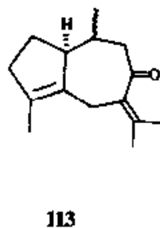


110. R = CH_2OH

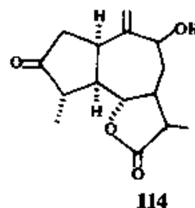
111. R = CHO



112



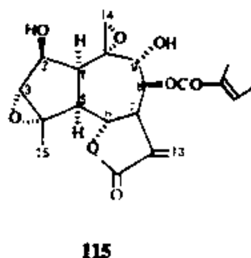
113



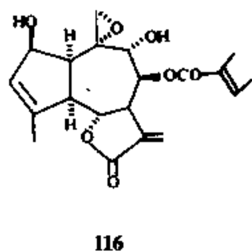
114

表 8-28　愈创木烷衍生物 115～120 的 ^{1}H-NMR 化学位移[25～29]

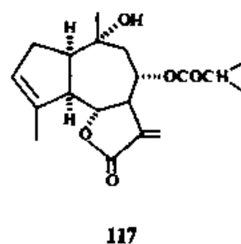
质子 \ 化合物	115	116	117	118	119	120
1-H	2.27dd	2.1m	2.60ddd	2.44m	—	2.95dd
2-H	3.91d	4.75m	2.26dd	1.70～1.95m	—	—
			2.08dd			
3-H	3.42s	5.68bs	5.52bs	2.44m	6.23q	5.59dd
				2.91m		
5-H	2.44dd	2.35dd	2.79dd	1.91d	3.52bd	2.45m
6-H	5.08dd	5.18dd	4.02dd	4.60t	3.75t	4.08dd
7-H	3.09dddd	3.22dddd	3.88dddd	2.37m	3.27tt	2.87bdd
8-H	5.62dd	5.46dd	5.21dd	4.26ddq	4.95dt	—
9-H_A	4.38d	3.99d	2.33dd	5.87dq	2.76dd	—
9-H_B	—	—	1.79bd	—	2.48dd	—
13-H_A	6.32d	6.13d	6.18d	1.25d	6.28d	6.23d
13-H_B	5.52d	5.48d	5.50d	—	5.68d	5.51d
14-H_A	3.04d	3.08d	1.24s	1.84bs	2.48b	4.98bs
14-H_B	2.75d	2.85d	—	—	—	4.96bs
15-H	1.71s	2.00bs	1.92bs	5.45bs	2.36b	5.47bs
				5.08bs		5.28dd
OCOR	6.89bq	6.89bq	2.64qq	—	—	—
	1.80bd	1.81bd	1.26d	—	—	—
	1.79bs	1.80bs	1.25d	—	—	—



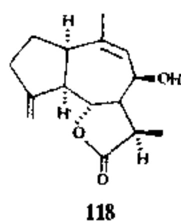
115

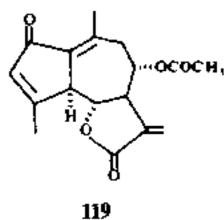


116



117


118


119

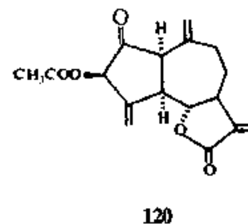
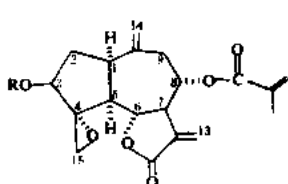
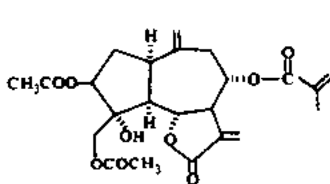

120

表 8-29 愈创木烷衍生物 121～124 的 ^{1}H-NMR 化学位移

质子＼化合物	121	122	123	124	质子＼化合物	121	122	123	124
1α-H	3.35ddd	3.41ddd	—	3.24ddd	11-H	—	—	—	2.48dq
2α-H	1.85ddd	1.85ddd	—	—	13-H$_A$	6.20d	6.24d	6.24d	1.25d
2β-H	2.47ddd	3.63ddd	—	—	13-H$_B$	5.60d	5.62d	6.69d	1.25d
3α-H	4.00dd	4.96dd	5.00m	4.02dd	14-H$_A$	5.19bs	5.20bs	5.18bs	5.29bs
5α-H	2.08dd	2.07dd	2.47dd	2.15m	14-H$_B$	4.96bs	4.99bs	5.15bs	5.09bs
6β-H	4.64dd	4.44dd	4.54dd	4.43dd	15-H$_A$	3.34d	3.34d	4.33d	3.39d
7α-H	3.10m	3.10m	3.20m	—	15-H$_B$	3.08d	3.10d	4.17d	3.06d
8β-H	5.13ddd	5.16ddd	5.00m	—	OCOCH$_3$	—	2.08s	2.08s	—
9α-H	2.77dd	2.70dd	—	—				2.14s	—
9β-H	2.42dd	2.45dd	—	—					


121. R = H
122. R = COCH$_3$


123

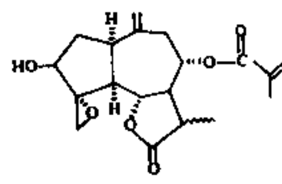
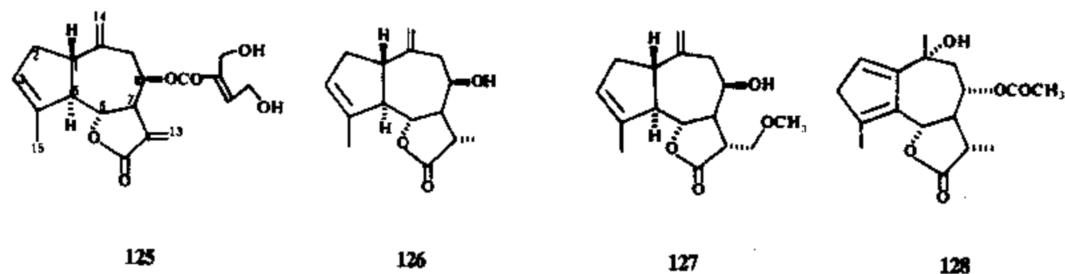

124

表 8-30 愈创木烷衍生物 125～128 的 ^{1}H-NMR 化学位移[31,32]

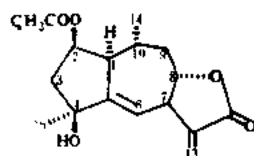
质子＼化合物	125	126	127	128	质子＼化合物	125	126	127	128
1-β-H	3.18m	3.17m	3.14m	—	11-β-H	—	3.04dt	2.84dq	2.62dt
2-H	2.47m	2.3～2.5m	1.94ddd	6.09t	13-H$_A$	6.26d	3.72d	1.25d	1.30d
			2.47m		13-H$_B$	5.54d	3.72d	1.25d	—
3-H	5.56bs	5.53bs	5.54bs	2.90dd	14-H$_A$	5.01bs	5.05bs	5.07bs	1.62s
5-α-H	2.84bdd	2.78bdd	2.75bdd	—	14-H$_B$	4.88bs	4.95bs	9.96bs	—
6-β-H	4.50dd	4.15dd	4.09dd	5.50d	15-H	1.87bs	1.84bs	1.84bs	2.19s
7-α-H	3.18m	2.87m	2.50ddd	—	OCOR	6.83t	—	—	—
8-α-H	5.64ddd	4.09m	4.01m	5.52m		4.38d	—	—	—
9-H	2.58d	2.47dd	2.43dd	1.66dd		4.31s	—	—	—
		2.58dd	2.63d	2.28dd	OCH$_3$	—	—	3.39s	—

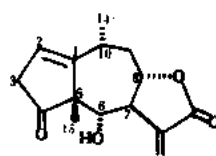


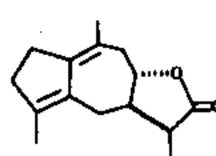
四、伪愈创木烷衍生物类化合物的¹H-NMR 化学位移

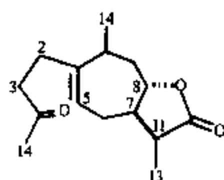
表 8-31 伪愈创木烷衍生物 129～134 的¹H-NMR 化学位移[33～36]

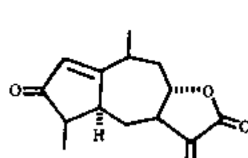
质子 \ 化合物	129	130	131	132	133	134
1-H	2.59ddd	—	—	—	—	2.71dd
2-H	5.07ddd	5.92ddd	2.25～2.5m	2.3～2.6m	6.05s	1.40～2.00m
3-H_A	1.74dd	3.08ddd	2.25～2.5m	2.3～2.6m	—	2.49bdd
3-H_B	2.39dd	2.90ddd	—	—	—	2.36ddd
5-H	—	—	—	5.37bdd	—	—
6-H	6.01dd	4.05dd	2.89bd	2.2～2.4m	—	2.64bd 1.54bdd
7-H	3.39dddd	3.09dddd	2.35m	2.2～2.4m	—	3.00m
8-H	3.82ddd	4.64ddd	4.18ddd	4.47ddd	3.90ddd	4.30ddd
9-H_A	1.70ddd	2.17ddd	1.90bdd	1.98ddd	—	2.36ddd
9-H_B	2.46ddd	1.82ddd	2.84bdd	1.87ddd	—	2.06dd
10-H	1.57m	2.71m	—	—	—	—
11-H	—	—	2.35m	2.25m	—	—
13-H_A	5.69d	6.10d	1.29d	1.22d	5.55d	6.25d
13-H_B	6.26d	6.40d	—	—	6.25d	5.57d
14-H_A	1.07d	1.32d	1.78bd	1.15d	1.15d	2.81d
14-H_B	—	—	—	—	—	3.04d
15-H	1.34s	1.26s	1.75bs	2.15s	1.35d	1.06s


129


130


131


132


133

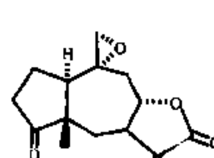
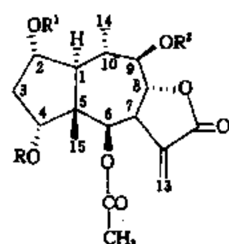
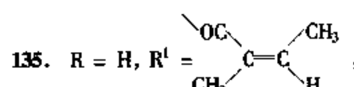

134

表 8-32 伪愈创木烷衍生物 135～139 的^{1}H-NMR 化学位移[37,38]

质子＼化合物	135	136	137	138	139
1-H	2.40dd	2.48dd	2.48dd	2.23dd	2.36dd
2-H	5.06ddd	5.13ddd	5.05ddd	5.08dddd	4.88ddd
3-$H_α$	2.65ddd	2.70ddd	2.70ddd	2.65ddd	2.72ddd
3-$H_β$	1.65dd	1.63dd	1.63dd	1.62dd	1.48dd
4-H	3.85d	4.85d	4.84d	3.86d	4.09d
6-H	6.04d	5.83d	5.82d	4.69d	3.71d
7-H	3.17dddd	3.32dddd	3.32dddd	2.44dddd	3.54dddd
8-H	4.58dd	4.64dd	4.63dd	4.56dt	4.82dt
9-H	3.34bt	4.91t	4.91t	3.19bt	1.88～2.12m
10-H	1.9m	2.08m	2.08m	1.9m	1.96m
11-H	—	—	—	2.17m	—
13-H_A	6.33d	6.32d	6.32d	3.59d	6.36d
13-H_B	5.51d	5.50d	5.50d	3.28m	5.85d
14-H	1.18d	1.00d	0.99d	1.17d	1.10d
15-H	0.83s	0.94s	0.95s	0.94s	0.93s
OCOR	6.09qq	6.11qq	0.93d	6.08dd	—
	2.00dq	1.99dq	—	2.00dq	—
	1.89dq	1.87dq	—	1.89dq	—



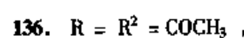
135. R = H, R^1 =

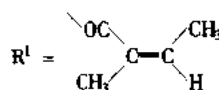


R^2 = H

136. R = R^2 = $COCH_3$,

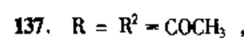
R^1 =

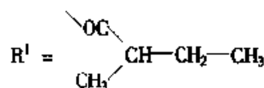


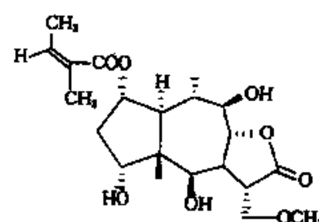


137. R = R^2 = $COCH_3$,

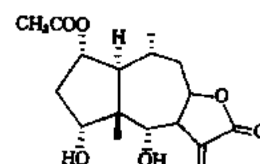
R^1 =







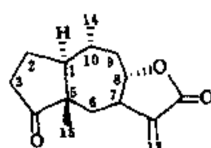
138

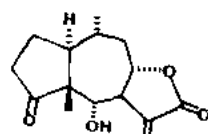


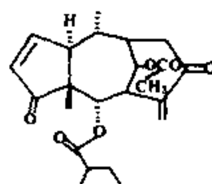
139

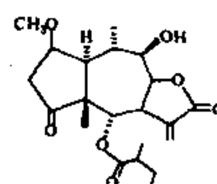
表 8-33 伪愈创木烷衍生物 140～143 的^{1}H-NMR 化学位移[39,40]

质子＼化合物	140	141	142	143
1-H	2.10ddd	2.15m	3.20dd	2.43m
2-$H_α$	2.20m	2.20m	7.61dd	4.02dd
2-$H_β$	1.60m	1.53m	—	—
3-$H_α$	2.20m	2.20m	6.10dd	2.68d
3-$H_β$	2.45m	2.45m	—	2.18dd
6-$H_α$	2.50dd	—	5.25d	5.16d
6-$H_β$	1.52dd	4.02dd	—	—
7-H	2.80dddd	2.89dddd	3.47bs	3.57m
8-H	4.28ddd	4.39ddd	5.44bs	4.96dd
9-$H_α$	1.42ddd	1.48ddd	4.65bs	3.57m
9-$H_β$	2.45m	2.46bd	—	—
10-H	1.93m	1.85m	2.41bdq	2.25dq
13-H_A	6.19d	6.22d	6.78dd	6.44d
13-H_B	5.51d	6.00d	6.06dd	6.15d
14-H	1.10d	1.11d	1.40d	1.28d
15-H	1.03s	1.04s	1.04s	0.99s







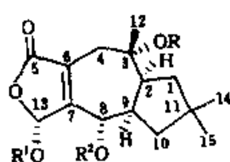


140　　141　　142　　143

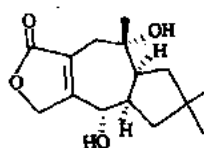
五、其他五·七环和三·七环倍半萜类化合物的¹H-NMR化学位移

表8-34　五·七环倍半萜类化合物144～151的¹H-NMR化学位移[41]

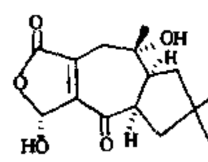
质子＼化合物	144	145	146	147	148	149	150	151
4-H_A	2.68dd	2.68	2.70dt	2.74	2.94d	2.82d	2.92～2.94	2.84d
4-H_B	2.50dd	2.68	2.52dt	2.74	2.78d	2.54d	—	2.52d
5-H	—	—	—	—	5.89d	6.72s	4.58s	4.64s
					5.97d	6.78s		
13-H	6.31t	6.9t	4.58dt	6.30t	—	—	—	—
			4.99dt					
8-H	4.28d	5.70d	4.10d	—	4.36d	5.84d	2.7m	4.62d
					4.39d			
12-H	1.26s	1.24s	1.30s	1.35s	1.26s	1.25s	1.28s	1.25s
14-H	1.04s	1.09s	1.04s	1.09s	1.00s	1.06s	1.02s	0.86s
15-H	1.02s	1.00s	1.02s	1.04s	1.00s	1.00s	1.00s	0.79s



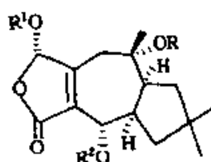
144. R = R¹ = R² = H
145. R = H, R¹ = R² = $COCH_3$



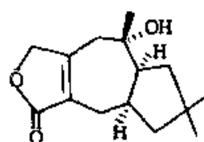
146



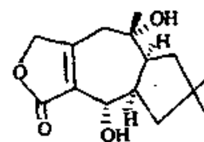
147



148. R = R¹ = R² = H
149. R = H, R¹ = R² = $COCH_3$



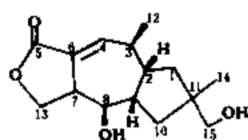
150



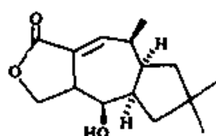
151

表 8-35　五·七环倍半萜类化合物 152～155 的 ^{1}H-NMR 化学位移[42]

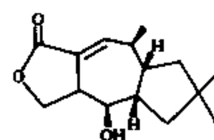
质子＼化合物	152	153	154	155	质子＼化合物	152	153	154	155
4-H	6.73t	6.67t	6.62dd	—	13-H	4.18t	4.11t	4.27dddd	4.15dd
7-H	3.40m	3.3m	3.62m	3.70m		4.57t	4.54t		4.65dd
8-H	3.62dd	3.66t	3.93dd	—	14-H	1.03s	1.00s	1.13s	1.22s
12-H	1.14d	1.11d	1.14d	10.5d	15-H	3.44s	1.08s	1.02s	1.07s



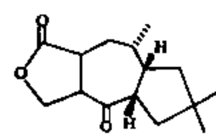
152



153



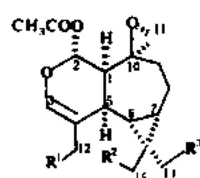
154



155

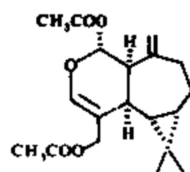
表 8-36　三·七环倍半萜类化合物 156～162 的 ^{1}H-NMR 化学位移[43]

质子＼化合物	156	157	158	159	160	161	162
1-H	1.73dd	2.77dd	1.78	—	1.67dd	3.18dd	4.96t
2-H	6.78bs	6.45d	6.68d	6.67d	6.73d	6.41d	2.31dd
3-H	6.30bs	5.88d	6.10bs	5.15bs	5.20bs	5.20bs	5.16t
5-H	—	—	—	—	—	—	4.63bd
6-H	—	0.7	0.5dd	—	—	—	—
11-H	2.45bs	4.72s	2.40bs	2.43bs	2.43s	4.78s	1.46d
12-H	4.50bs	1.55d	3.92s	4.97bs	4.90bs	5.00bs	1.67d
					5.08bs		
14-H	3.26d	1.02s	1.07s	1.05s	1.07s	1.06s	1.03s
	3.61d						
15-H	4.38bs	1.05s	1.07s	1.13s	1.12s	1.15s	1.08s
$OCOCH_3$	2.16s	2.05s	2.17s	2.17s	2.17s	2.10s	2.00s
OCH_3	—	—	—	3.45s	3.52s	3.50s	—

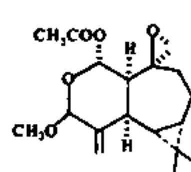


156. $R^1 = R^2 = OCOCH_3$, $R^3 = OH$

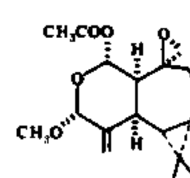
158. $R^1 = OH$, $R^2 = R^3 = H$



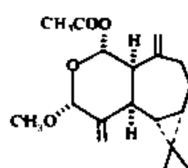
157



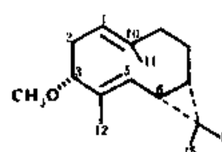
159



160



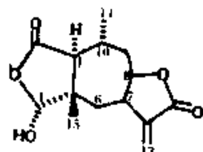
161



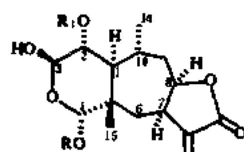
162

表 8-37 七环倍半萜类化合物 163 ~ 168 的^{1}H-NMR 化学位移[44]

质子 \ 化合物	163	164	165	166	167	168
1-H	2.54d	2.0m	2.0m	2.0m	2.0m	1.8m
2-H	—	4.94dd	5.07dd	4.91dd	5.07dd	5.50d
3-H	—	5.07bd	4.91d	4.81dd	4.79d	—
4-H	5.28bs	4.68bs	4.70bs	4.10s	4.68d	5.53s
6-H$_{\alpha}$	2.12dd	—	—	—	—	1.74dd
6-H$_{\beta}$	1.59dd	—	—	—	—	2.96dd
7-H	3.47m	3.46m	3.44m	3.36m	3.4m	3.14m
8-H	4.82ddd	4.75ddd	4.75ddd	4.71ddd	4.72ddd	5.34ddd
9-H	1.99m	1.83bd	—	1.83bd	1.82bd	1.8m
10-H	2.09m	1.99m	—	2.0m	2.0m	2.1m
13-H$_A$	6.30d	6.23d	6.23d	6.22d	6.21d	6.35d
13-H$_B$	5.67d	5.63d	5.60d	5.53d	5.57d	5.77d
14-H	1.38d	1.18d	1.10d	1.17d	1.14d	1.07d
15-H	1.13s	1.15s	1.19s	1.17s	1.16s	1.44s
OCOCH$_3$	—	2.12s	—	2.10s	2.06s	2.11s
OCH$_2$CH$_3$	—	—	3.79dq	—	—	3.88dq
			3.50dq			3.64dq
OH	4.35bs	2.96bs	2.70bs	2.80d	1.81d	—
OCH$_3$	—	—	—	3.49s	3.49s	—



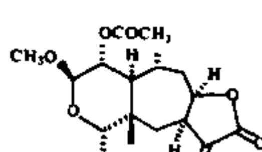
163



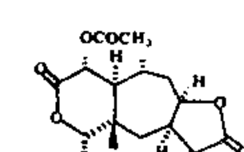
164. R = H, R^1 = COCH$_3$

165. R = CH$_2$CH$_3$, R^1 = CO—C(CH$_3$)═C(H)CH$_3$

166. R = CH$_3$, R^1 = COCH$_3$



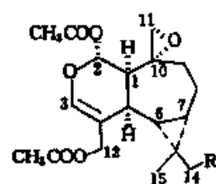
167



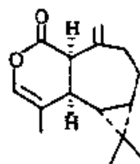
168

表 8-38 三·七环倍半萜类化合物 169 ~ 175 的^{1}H-NMR 化学位移[45,46]

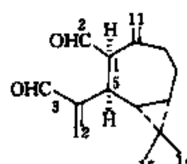
质子 \ 化合物	169	170	171	172	173	174	175
1-H	1.70dd	1.77dd	3.53d	—	—	—	—
2-H	6.79d	6.93d	—	9.67d	7.06bt	2.68dd	—
3-H	6.28d	6.47bs	6.24d	9.57s	9.61s		—
5-H	2.10dd	—	1.90dd	—	3.75d	—	—
6-H	0.55dd	0.8dd	0.43dd	—	0.90dd		
7-H	0.90m	—	0.84m	—	—	5.56dd	5.40m
8-H	1.1 ~ 2.1m	—	0.86m	—	—	5.49d	5.75d
			2.05m				
9-H	1.0 ~ 2.0m	—	2.50m	2.20m	2.80m	—	—
10-H$_A$	—	—	—	—	—	5.24bs	5.30bs
10-H$_B$	—	—	—	—	—	4.83d	4.94bs
11-H$_A$	2.42d	2.55bs	4.76d	4.50s	—	—	—
11-H$_B$	2.48dd	2.55bs	4.92bs	4.85d	6.53bs	—	—
12-H$_A$	4.40d	4.13d	—	6.20s	6.21s	3.28d	3.16d
12-H$_B$	4.40d	4.49d	1.74d	6.52s	6.55s	3.18d	3.06d
14-H	1.07s	4.60bs	1.06s	1.00s	1.06s	5.00m	4.94m
15-H	1.02s	1.20s	1.06s	1.16s	1.06s	1.24d	1.23d
OCH$_3$	—	—	—	—	—	3.76s	3.73s
OCOCH$_3$	2.03s	2.15s	—	—	—	2.08s	2.09s
	2.19s	2.20s	—	—	—	—	—



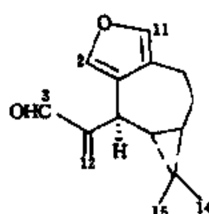
169. R = H
170. R = OCOCH₃



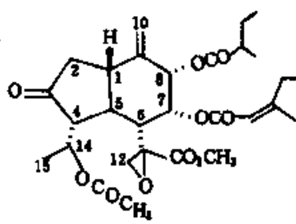
171



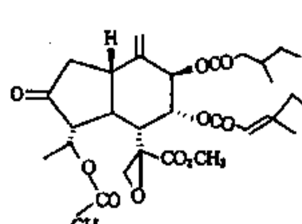
172



173



174

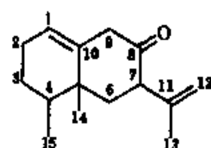


175

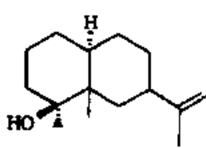
六、佛木烷衍生物的^{1}H-NMR化学位移

表 8-39 佛木烷衍生物 176～181 的^{1}H-NMR 化学位移[47～50]

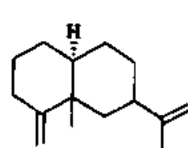
质子 \ 化合物	176	177	178	179	180	181
1-H	5.48m	—	—	—	—	1.38ddd
2-H	2.07m	—	—	—	—	4.91dddd
3-$H_α$	1.6m	2.06dddd	2.28bd	5.32b	4.15ddd	—
3-$H_β$	1.6m	1.33m	2.00dd	—	—	—
4-H	1.6m	—	—	—	—	1.65m
6-$H_α$	1.93dd	1.75m	—	1.85m	5.72s	2.79d
6-$H_β$	1.65dd	1.75m	—	1.85m	—	1.9m
7-H	2.88dd	2.43b	2.41b	2.41b	—	—
9-$H_α$	3.17dddd	—	—	—	2.20bd	2.20dd
9-$H_β$	2.80d	—	—	—	2.44dd	—
11-H	—	—	—	—	2.93q	—
12-H_A	4.94bs	4.92dq	4.90dq	4.92dq	—	—
12-H_B	4.73bs	4.87dq	4.82bs	4.85dq	—	—
13-H	1.71bs	1.75bs	1.73bs	1.76bs	1.26d	1.82d
14-H	1.04s	0.93s	0.76s	0.86s	0.98s	1.12s
15-H	0.97d	1.09s	4.69ddd 4.43ddd	1.62ddd	0.91d	0.88d



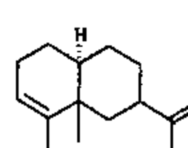
176



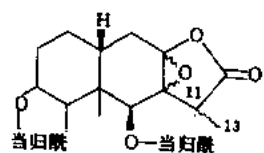
177



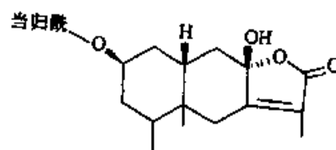
178



179



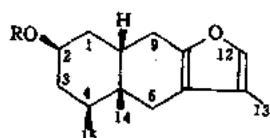
180

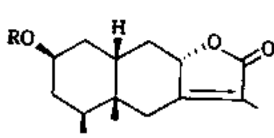


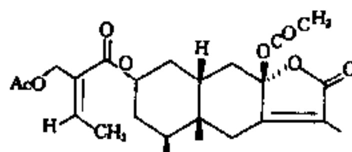
181

表 8-40　佛木烷衍生物 182～187 的¹H-NMR 化学位移[48,50]

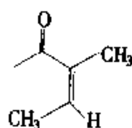
质子 \ 化合物	182	183	184	185	186	187
1-H_α	—	—	1.38ddd	1.37ddd	1.37dddd	—
2-H	5.19dddd	5.19dddd	4.94ddd	4.98dddd	4.93dddd	—
4-H	1.60m	1.60m	1.66m	1.65m	1.65m	—
6-H_α	2.45d	2.43d	2.92d	2.93d	2.86d	—
6-H_β	1.9m	1.9m	1.90m	1.93bd	1.9m	—
8-H	—	—	4.62dd	4.62dd	—	4.80m
9-H_α	2.58dd	2.57dd	2.29ddd	2.30ddd	2.51dd	—
9-H_β	2.44dd	2.44dd	1.85m	1.85m	1.87dd	—
10-H	—	—	1.85m	1.85m	1.85m	—
12-H	7.04bs	7.04bs	—	—	—	1.85d
13-H	1.83d	1.84d	1.81bs	1.82bs	1.86d	—
14-H	0.86s	0.87s	1.11s	1.11s	1.11s	1.15s
15-H	0.84d	0.82d	0.87d	0.89d	0.90d	4.96bs
						5.18bs
OCOR	5.79qq	6.03tq	6.02qq	6.39tq	6.40tq	—
	2.00dq	1.99tq	1.96dq	2.08tq	2.08tq	—
	1.91dq	4.21bs	1.86dq	4.71bs	4.72bs	—

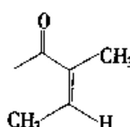


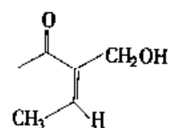


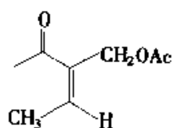


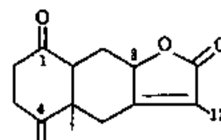
186

182. R =


184. R =


183. R =


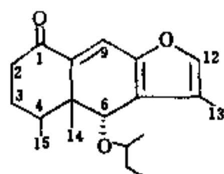
185. R =




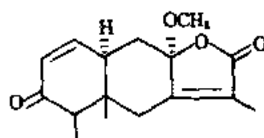
187

表 8-41　佛木烷衍生物 188～193 的^{1}H-NMR 化学位移[51～53]

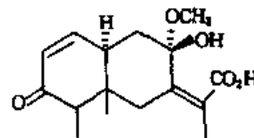
质子 \ 化合物	188	189	190	191	192	193
1-H	—	6.54dd	6.53dd	1.58m 1.43m	—	—
2-H	2.65ddd	6.07dd	6.03dd	—	—	—
	2.40ddd	—				
3-H	1.85m	—	—	—	5.35ddd	5.29ddd
4-H	2.28m	2.50q	2.45q	1.98m	—	—
6-$H_α$	—	2.66d	2.41d	—	5.04bs	5.04bs
6-$H_β$	5.84s	2.16bd	1.85bd	4.64bs	—	—
9-$H_α$	7.45s	2.46dd	2.26dd	2.66dd	2.84bd	2.84bd
9-$H_β$	—	1.72dd	1.62dd	2.49dd	2.23bd	2.23bd
10-H	—	3.02ddd	2.95ddd	2.20ddd		
11-H	—	—	—	—	—	—
12-H	7.25bs	—	—	7.03bs	7.05bs	7.05bs
					—	—
13-H	2.07bs	1.89d	1.76bs	2.04d	2.08bs	2.08bs
14-H	1.02s	0.65s	0.60s	1.16s	0.95s	0.95s
15-H	1.02d	1.16d	1.11d	3.92dd	0.99d	0.98d
				3.55dd		
OCOR	2.46qq	—	—	—	6.86qq	5.69qq
	1.14d	—	—	—	1.80dq	2.17d
	1.09d	—	—	—	1.84dq	1.90d
OCH_3	—	3.16s	3.19s	—	—	—



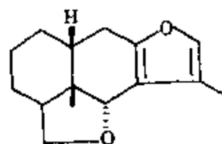
188



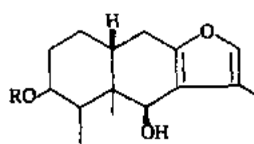
189



190



191



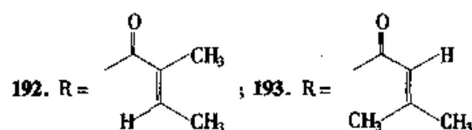
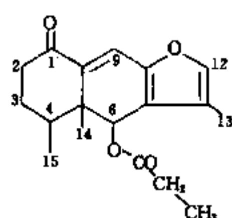
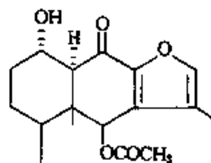


表 8-42　佛木烷衍生物 194～199 的^{1}H-NMR 化学位移[47,54]

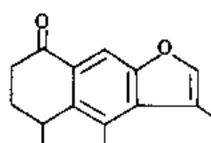
质子 \ 化合物	194	195	196	197	198	199
1-H	—	4.16dddd	—	3.07dd	3.10d	—
2-$H_α$	2.46ddd	—	2.63ddd	1.97m	1.84m	—
2-$H_β$	2.58ddd	—	2.89ddd	1.97m	2.03m	—
3-$H_α$	1.78m	—	2.30dddd	1.33m	1.34m	5.34ddd
3-$H_β$	—	—	2.07dddd	1.23m	1.70m	—
4-H	2.13m	1.90m	3.47ddq	1.79ddq	1.50ddq	—
6-$H_α$	6.53s	6.35s	—	2.27bdd	2.25d	6.47bs
6-$H_β$	—	—	—	2.42dd	2.70bd	—
9-$H_α$	7.21s	—	8.04s	3.22dddd	2.12d	2.31bd
9-$H_β$	—	—	—	2.11dd	3.13bd	2.87bdd
10-H	—	2.38d	—	—	—	—
12-H	7.20q	7.40q	7.46q	7.08bs	7.07bs	7.04bs
13-H	1.88d	1.92d	2.43d	1.92d	1.92d	1.85d
14-H	1.19s	0.97s	2.67s	0.93s	1.13s	1.04s
15-H	0.97d	0.91d	1.33d	0.85d	1.10d	0.95d
OCOR	2.46q	2.18s	—	—	—	6.10qq
	1.23t	—	—	—	—	2.02dq
	—	—	—	—	—	1.93dq



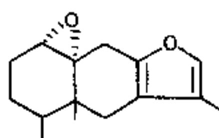
194



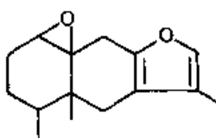
195



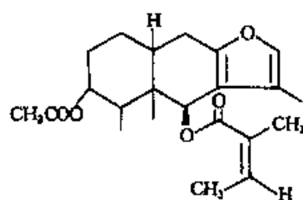
196



197



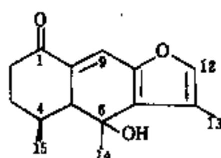
198



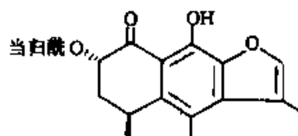
199

表 8-43 佛木烷衍生物 200～206 的^{1}H-NMR 化学位移[55,56]

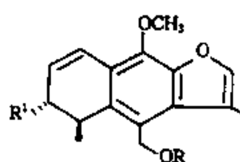
质子 \ 化合物	200	201	202	203	204		205	206
1-H	—	—	7.14d	6.93dd	8.29	2.93dd	4.72dd	4.85dd
						2.59dd		
2-H_α	2.64m	—	6.15dd	5.94dd	7.31dd	1.80m	1.66m	1.66m
2-H_β	2.98m	6.05dd	—	—	—	—	2.33m	2.33m
3-H_α	1.80m	2.46ddd	—	2.55dddd	7.22bd	1.80m	2.33m	2.33m
3-H_β	1.80m	2.30ddd	4.11bd	2.24ddd	—	—	1.42m	1.42m
4-H	1.80m	3.58ddq	3.59bq	3.34bdq	—	3.21ddq	1.74m	1.74m
6-H	—	—	—	—	—	—	7.04s	7.05s
9-H	7.53s	—	—	—	—	—	—	—
12-H	7.42q	7.51q	7.39q	7.36q	7.44q	—	7.47q	7.41q
13-H	2.25d	2.41d	2.34d	2.33d	2.29d	2.12s	1.98d	1.92d
14-H	1.60s	2.54s	5.47d	5.43d	4.99bs	2.49s	1.02s	1.01s
			5.41d	5.37d	2.85bs	1.18d	1.18d	1.19d
15-H	1.40d	1.45d	1.80d	1.11d	—	4.85s	3.94s	3.98s
OH	—	12.97s	—	—	—	—	2.23s	2.20s
$OCOCH_3$	—	—	—	2.10	—	—	2.20s	5.92qq
OCOR	—	6.19qq	5.70qq	—	—	—	0.90d	1.89dq
	—	2.08dq	2.20d	—	—	—	0.87d	1.56dq
	—	2.00dq	1.88d	—	4.31s	—	—	—
OCH_3	—	—	4.18s	—				

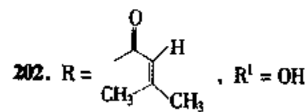


200



201

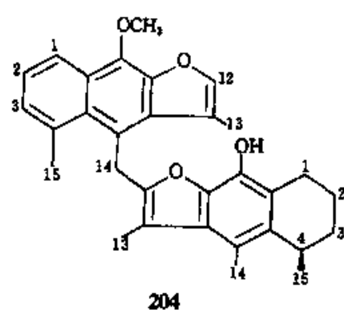




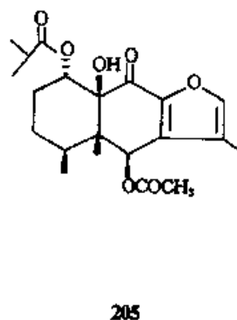
202. R = , R^1 = OH



203. R = $COCH_3$, R^1 = H



204


205

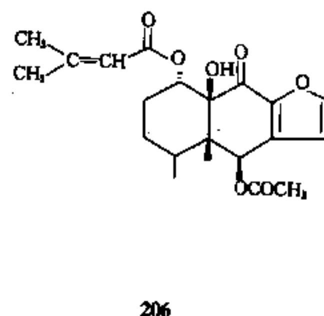
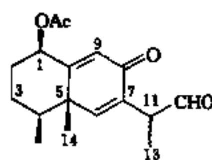

206

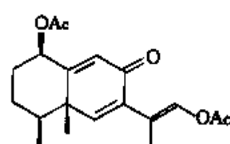
表 8-44 佛木烷衍生物 207～212 的 ^{1}H-NMR 化学位移①[126]

质子＼化合物	207	208	209	210	211	212
1-H	5.49t(3.0)	5.49t(3.0)	5.48t(3.0)	5.50t(3.0)	4.56t(2.8)	5.44t(3.0)
2-H	2.12dddd (14.0,4.0, 4.0,3.0)	2.12dddd (14.0,4.0, 4.0,3.0)	2.13m	2.13m	2.09dddd (13.5,4.0, 4.0,3.2)	2.03dddd (13.5,4.0, 4.0,3.2)
2′-H	1.85dddd (14.0,14.0 14.0,3.0)	1.85dddd (14.0,14.0 14.0,3.0)	1.86dddd (14.0,14.0, 14.0,3.0)	1.86dddd (14.0,14.0, 14.0,3.0)	2.02dddd (13.5,13.5, 13.5,3.2)	2.03dddd (13.5,13.5, 13.5,3.2)
3-H	1.46m	1.46m	1.48m	1.49m	1.52m	1.56m
3′-H	1.58m	1.58m	1.60m	1.62m	1.61m	1.73m
4-H	1.71m	1.71m	1.70m	1.71m	1.68m	1.96m
6-H	6.79s	6.81s	6.88s	7.67s	7.68s	3.52s
9-H	6.37s	6.37s	6.36s	6.31s	6.18s	6.06s
11-H	3.72q(6.0)	3.67q(6.0)	—	—	—	—
12-H	9.66s	9.66s	7.41s	—	—	—
13-H	1.27d(6.0)	1.27d(6.0)	1.92d(1.1)	2.56s	2.56s	2.35s
14-H	1.26s	1.26s	1.26s	1.29s	1.38s	1.30s
15-H	1.16d(6.4)	1.16d(6.4)	1.13d(6.6)	1.15d(6.6)	1.15d(6.6)	1.15d(6.7)
OAc	2.06s	2.06s	2.06s 2.18s	2.06s	—	2.06s

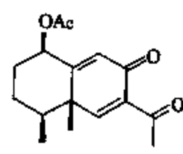
① 括号内为 *J* 值。



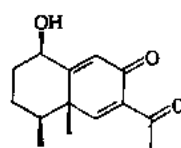
207. 11 * *S*
208. 11 * *R*



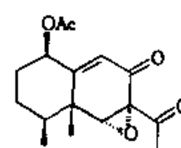
209



210



211

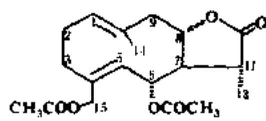


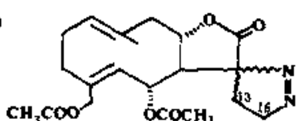
212

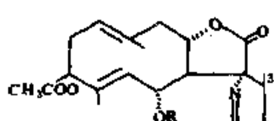
七、吉马烷衍生物的^{1}H-NMR化学位移

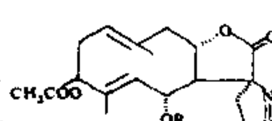
表 8-45　吉马烷衍生物 213～219 的^{1}H-NMR 化学位移[57,58]

质子＼化合物	213	214	215	216	217	218	219
1-H	4.98m	5.10m	4.98m	5.22bdd	5.21bdd	5.15bd	5.21bd
2-H_α	2.22m	2.24m	2.24m	2.45m	2.43m	2.50ddd	2.50ddd
2-H_β	—	1.9m	1.9m	2.45m	2.43m	2.36bd	2.37bd
3-H_α	2.45m	2.5ddd	2.47ddd	5.22dd	5.29dd	5.18dd	5.31dd
3-H_β	—	1.9m	1.9m	—	—	—	—
5-H	4.84bd	—	4.70bd	5.05bd	4.99bd	4.93bd	4.85bd
6-H	5.44dd	5.39dd	5.61dd	4.37t	5.46t	4.57t	5.68t
7-H	2.22m	3.79dd	2.79dd	3.46t	3.85t	2.59t	2.86t
8-H	4.14dd	4.22bdd	5.02dd	4.37t	4.45ddd	5.02ddd	5.06ddd
9-H_α	2.45m	2.66dd	2.55dd	2.64dd	2.68dd	2.52m	2.58dd
9-H_β	2.84bd	3.05bd	3.06bd	2.99bd	3.05bd	3.04bd	3.04bd
11-H	2.59dq	—	—	—	—	—	—
13-H_A	1.40d	2.3m	2.31m	2.15ddd	1.87m	2.15ddd	2.32ddd
13-H_B	—	1.9m	1.90m	1.75ddd	1.67m	1.92ddd	1.89ddd
14-H	1.50bs	1.47bs	1.58bs	1.51bs	1.54bs	1.58bs	1.64bs
15-H	4.73d	4.74d	4.78d	1.68bs	1.76bs	1.64bs	1.77d
	4.59d	4.66d	4.72d				
16-H_A	—	4.70m	4.84dd	4.91ddd	4.77ddd	4.85ddd	4.85ddd
16-H_B	—	—	4.70m	4.73ddd	4.66ddd	4.72ddd	4.67ddd
$OCOCH_3$	2.09s	1.85s	1.87s	2.07s	1.84s	2.08s	1.86s









213　　214. α-加成物　215. β-加成物　216. R = H　217. R = $COCH_3$　218. R = H　219. R = $COCH_3$

表 8-46　吉马烷衍生物 220～226 的^{1}H-NMR 化学位移[59]

质子＼化合物	220	221	222	223	224	225	226
1-H	—	—	—	—	—	4.49	4.51
2-H	6.61	6.61	6.57	6.61	6.67	5.34	5.34
3-H	6.03	6.02	5.79	6.00	6.17	5.34	5.34
4-H	3.13	—	3.10	3.08	3.27	3.60	3.57
5-H_α	1.83	—	—	1.85	—	1.7～1.8	1.81
5-H_β	1.44	—	—	1.44	—	1.7～1.8	1.68
6-H	4.62	4.57	4.56	4.50	4.56	4.75	4.74
7-H	2.66	2.63	2.62	2.52	2.73	4.34	4.34
8-H	5.62	5.57	5.66	4.14	5.43	5.51	5.52
9-H	5.62	5.57	5.54	5.54	3.97	5.44	5.44
11-H	—	—	—	—	—	2.86	2.84
13-H_A	5.84	5.82	5.70	5.71	5.73	1.09	1.11
13-H_B	6.32	6.31	6.28	6.31	6.33	—	—
14-H	1.35	1.34	1.32	1.32	1.53	1.28	1.30
15-H	1.14	1.13	1.11	1.13	1.13	1.04	1.05
OCOR	5.54	—	—	6.69	—	5.60	5.59
	6.01	—	—	6.25	—	6.07	6.08
	1.83	—	—	2.00	—	1.85	1.87
	2.01	2.09	1.99	—	2.02	1.93	1.94

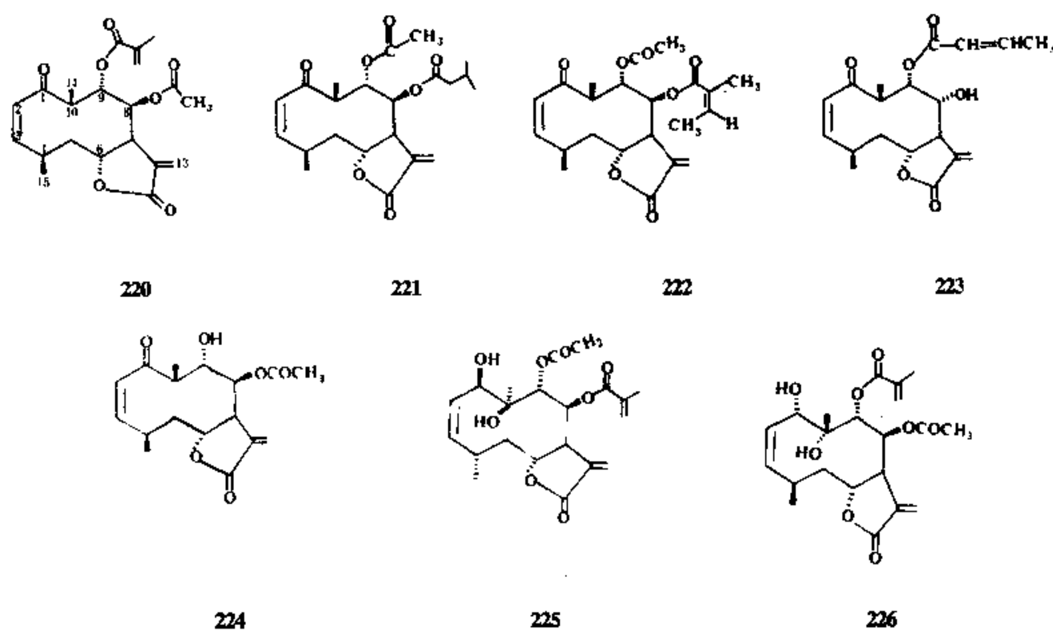
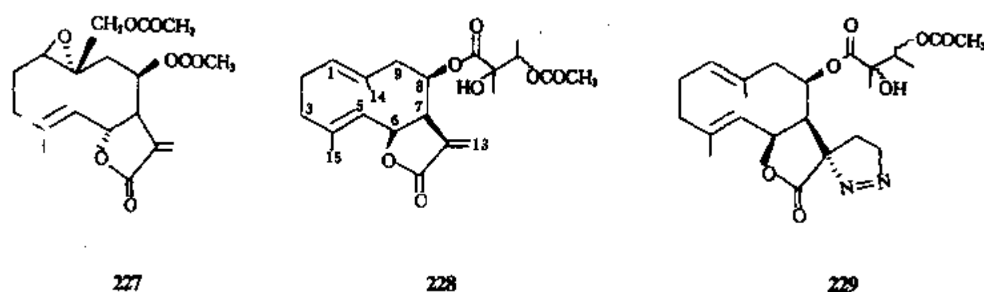
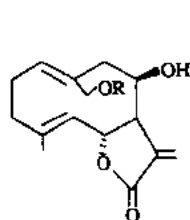
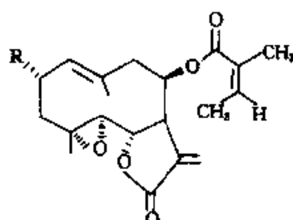


表 8-47 吉马烷衍生物 227 ~ 234 的^{1}H-NMR 化学位移[60~63]

化合物 质子	227	228	229	230	231	232	233	234
1-H	2.86dd	4.98m	5.13bdd	5.06dd	5.14dd	5.28bd	5.37bd	5.28bd
2-H	2.30m	2.3 ~ 2.0m	2.2 ~ 2.4m	2.1 ~ 2.4m	2.1 ~ 2.4m	—	4.70dt	5.64dt
3-H	2.30m	2.0 ~ 2.3m	2.2 ~ 2.4m	2.1 ~ 2.4m	2.1 ~ 2.4m	—	—	—
5-H	5.43bd	5.35m	5.46bd	4.86bd	4.85bd	2.82d	2.92d	2.90d
6-H	5.08dd	5.35m	6.27dd	5.12m	5.20m	4.41t	4.39t	4.39d
7-H	3.00m	3.42m	2.84d	2.78m	2.76m	3.16m	3.22m	3.16m
8-H	5.72bd	5.35m	5.27dd	4.49d	4.59d	5.72bd	5.78bd	5.78bd
9-H_α	1.16bd	2.73bd	2.65bd	2.89dd	2.94dd	—	—	—
9-H_β	3.19dd	2.39dd	2.27dd	2.40bd	2.20bd	—	—	—
13-H_A	6.21d	6.40d	2.24m	6.36d	6.36d	6.33d	6.37d	6.38d
13-H_B	5.10d	5.78d	1.60m	5.61d	6.36d	5.70d	5.72d	5.72d
14-H_A	3.84bd	1.44bs	1.49d	4.14bd	4.80bd	1.73bs	1.79bs	1.88bs
14-H_B	4.04d	1.44bs	1.49d	3.83bd	4.58bd	—	—	—
15-H	1.86bs	1.75bs	1.83d	1.68s	1.63s	1.35s	1.34s	1.38s
16-H_A	—	—	4.99ddd	—	—	—	—	—
16-H_B	—	—	4.62ddd	—	—	—	—	—
OCOR	—	1.40bs	1.40s	—	—	6.10qq	6.12qq	6.13qq
	—	1.18bd	1.27d	—	—	1.94dq	1.95dq	1.96dq
	—	5.30m	5.01q	—	—	1.82m	2.01m	1.83m







230. R = H

231. R = $COCH_3$

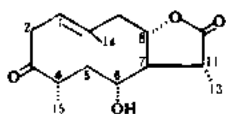
232. R = H

233. R = OH

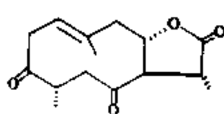
234. R = $OCOCH_3$

表 8-48 吉马烷衍生物 235～242 的¹H-NMR 化学位移[64,65]

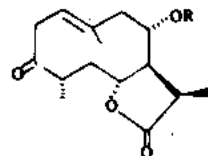
质子 \ 化合物	235	236	237	238	239	240	241	242
1-H	5.62tq	5.64bt	5.52tq	5.48bt	5.71bt	2.60d	2.60d	2.63d
2-H	3.13bd	3.07bd	3.27dd	3.28dd	3.20bd	3.00dd	3.05dd	3.06dd
			3.13bdd	3.11bdd				
4-H	2.90ddq	3.22ddq	2.71ddq	2.71ddq	2.28ddq	3.97dt	3.80bd	3.83bd
5-$H_α$	1.63ddd	2.58dd	2.32bdd	2.35bdd	1.77ddd	4.12d	5.39d	3.23bd
5-$H_β$	1.80ddd	2.67dd	1.76ddd	1.81m	1.96ddd	—	—	—
6-H	3.08ddd	—	3.86m	3.77m	4.15ddd	4.38d	4.46d	4.53d
7-H	2.15bdd	2.98dd	2.04ddd	1.81m	3.01m	2.92bd	2.95bd	2.93bd
8-H	4.29ddd	4.81ddd	4.99ddd	3.80ddd	—	5.11ddd	5.10ddd	5.14ddd
9-$H_α$	2.19dd	2.16dd	2.30dd	2.33dd	3.28bd	1.34dd	1.34dd	1.43dd
9-$H_β$	2.94bdd	2.86bdd	2.65bdd	2.63bdd	3.18bd	2.57dd	2.59dd	2.63dd
11-H	3.18dq	2.60dq	2.42dq	2.82dq	3.01m	—	—	—
13-H_A	1.34d	1.36d	1.33d	1.36d	1.28d	5.67bs	5.70bs	5.67bs
13-H_B	—	—	—	—	—	6.31bs	6.37bs	6.30bs
14-H	1.68bs	1.50bs	1.78bs	1.74bs	1.78bs	1.58s	1.60s	1.64s
15-H_A	1.11d	1.19d	1.16d	1.17d	1.09d	5.29bs	5.44bs	3.29d
15-H_B	—	—	—	—	—	5.53bs	5.63bs	2.73bd
OCOR	—	—	—	—	—	6.08qq	6.09qq	6.11qq
	—	—	—	—	—	1.93dq	1.93dq	1.94dq
	—	—	—	—	—	1.79dq	1.78dq	1.80dq



235

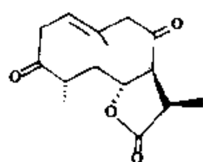


236

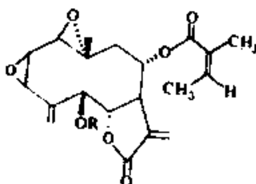


237. R = $COCH_3$

238. R = H

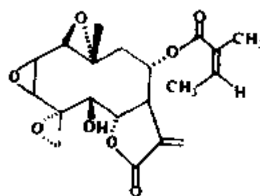


239



240. R = H

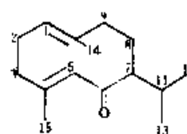
241. R = $COCH_3$



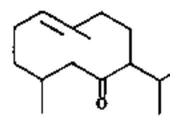
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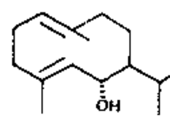
表 8-49 吉马烷衍生物 243～250 的^{1}H-NMR 化学位移[66~68]

质子 \ 化合物	243	244	245	246	247	248	249	250
1-H	4.87bdd	5.22bt	4.79m	—	—	—	5.01dd	6.26dd
2-H	2.15m	2.2m	—	—	—	—	—	—
3-H	2.42ddd	1.3～1.5m	—	2.37m	2.32m	2.65m	—	—
5-H	5.62bs	2.0～2.54m	4.79m	5.52bd	5.43bd	5.81bs	4.81bd	4.99bd
6-H	—	—	—	5.31bd	4.07bd	—	4.55dd	4.44dd
7-H	2.2m	1.97ddd	—	—	—	—	2.60m	3.06m
8-H	1.7～1.9m	1.3～1.5m	—	—	—	—		
9-H	2.2m	2.0m		—	—	—		
11-H	2.12m	1.56dqq	—	1.87qq	1.80qq	1.78qq		
12-H	0.96d	0.81d	0.81d	1.06d	1.00d	0.97d		
13-H	0.90d	0.84d	0.95d	0.97d	0.94d	0.94d	5.54d	5.54d
							6.28d	6.28d
14-H$_A$	1.20bs	1.55bs	1.44bs	1.08s	1.00s	1.20s	3.80d	9.95s
14-H$_B$	—	—	—	—	—	—	4.23d	—
15-H	2.00d	1.18d	1.63bs	1.70bs	1.70bs	1.88bs	1.62d	1.56bs

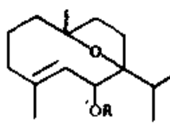


243

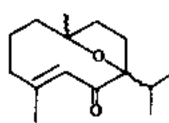

244

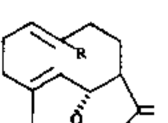


245



246. R = COPh
247. R = H

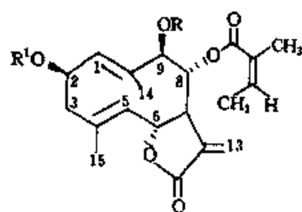

248



249. R = CH_2OH
250. R = CHO

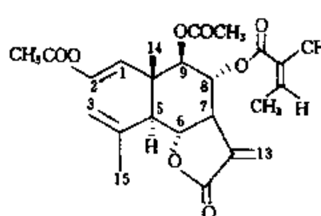
表 8-50 吉马烷衍生物 251～258 的^{1}H-NMR 化学位移[69~71]

质子 \ 化合物	251	252	253	254	255	256	257	258
1-H	5.60	5.77	4.42d(7.5)	5.05bd	5.04bd	5.08bd	5.52bdd	5.43bdd
2-H	4.92bs(8)	—	6.99d(7.5)	4.84dt	5.71dt	4.79	2.40m	2.44m
3-H$_A$	2.72dd (13,8)	2.78dd (14,7)	5.11t(1.5)	—	—	—	—	—
3-H$_B$	2.36d(13)	2.33d(10)	4.82d	—	—	—	—	—
5-H	4.95d(11)	4.96d(10)	2.95d(11)	5.12bd	5.04bd	5.08	4.10bdd	5.10bdd
6-H	5.33dd (10,8)	5.33dd (10,8)	4.26dd (11,5)	5.20dd	5.20dd	5.15	—	—
7-H	2.75m	2.69m	3.02m	2.95m	3.00m	2.98	2.77m	2.87m
8-H	4.54dd (10,3)	4.78dd (10,3)	5.51dd (7,6)	5.88m	5.90m	5.85	4.15ddd	4.27ddd
9-H$_\alpha$	4.19dd (10,4)	5.14d(10)	5.61d(7)	2.76dd	2.79dd	2.77	2.80dd	2.79dd
9-H$_\beta$	—	—	—	2.38dd	2.38dd	2.09	2.06dd	2.05m
13-H$_A$	6.09d(3.8)	6.23d(3.8)	6.11d(3)	6.33d	6.36d	6.36	6.32dd	6.33d
13-H$_B$	5.64d(3.5)	5.61d(3.5)	5.43d(3)	5.65d	5.66d	5.65	6.19dd	5.77d
14-H	1.93s	1.87s	1.36s	1.86bs	1.84	1.82	1.73bs	1.77bs
15-H$_A$	1.86bs	1.87bs	1.86bs	1.53bs	1.63bs	1.59	5.34bs	5.24bs
15-H$_B$	—	—	—	—	—	—	5.18bs	5.22bs
OCOR	6.10bs	6.10bs	6.18bs	6.42bq	6.44	3.06q	—	—
	1.9～2.0m	1.9～2.1m	2.01m	4.39bd	4.34	—	—	—
	1.9～2.0m	1.9～2.1m	1.86m	5.22bd	4.20	—	—	—
	—	—	—	2.02bd	2.05	1.26	—	—

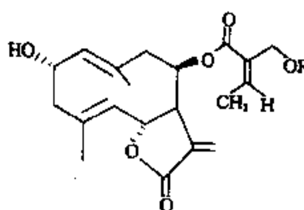


251. R = R¹ = H

252. R = R¹ = COCH₃

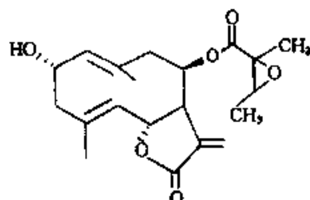


253

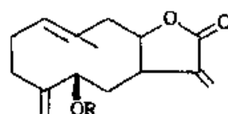


254. R = H

255. R = COCH₃



256



257. R = H

258. R = COCH₃

表 8-51　吉马烷衍生物 259 ~ 266 的^{1}H-NMR 化学位移[72~74]

质子 \ 化合物	259	260	261	262	263	264	265	266
1-H	5.20m	5.12m	5.06bd	—	4.51d	—	4.30dd (3.1)	4.92m
2-H	2.48m	2.2m	2.62dd	6.61d	5.34bs	6.61d(12)	5.14dd (12,3)	2.2 ~ 2.5m
3-H	2.48m	2.2m	5.22dd	6.03dd	5.34bs	6.01dd (12,11)	4.90dd (12,10)	5.23bdd
4-H	—	—	—	3.13m	3.57m	3.13m	3.58m	—
5-H	5.92d	4.52d	5.27d	1.84ddd 1.45ddd	1.81ddd 1.68ddd	—	1.2 ~ 1.48m	4.90bd
6-H	5.27dd	1.57d	4.48bt	4.62dd	4.74dd	4.59dd (11,5)	4.70dd (9.6)	4.58dd
7-H	—	0.96dd	—	2.65bs	4.34bd	2.65bs	4.20bs	2.53m
8-H	5.12ddd	4.88ddd	1.6m	5.62bs	5.52bd	5.70dd (10,2)	5.71dd (9,1.5)	—
9-H	2.1m 2.48m	1.85dd 2.81dd	2.1m 2.62m	5.62bs	5.44d	5.58d(10)	5.54d(9)	—
11-H	1.9m	—	2.0m	—	2.84dq	—	—	—
12-H	0.83d	1.12s	1.10d	—	—	—	—	—
13-H$_A$	0.78d	1.08s	1.05d	6.33d	1.11d	6.31d(1.5)	1.16d(7)	6.30d
13-H$_B$	—	—	—	5.54d	—	5.83d(1.5)	—	5.50d
14-H	1.68bs	1.55bs	1.49bs	1.36s	1.30s	1.34s	1.10s	1.47s
15-H	4.85s	1.69d	1.69d	1.15d	1.05d	1.12d(6.5)	0.84d(7)	1.72d
OCOR	6.05qq	6.12qq	6.93qq	6.03bs	6.08dq	6.04qq (7.5,1.8)	—	—
	1.99dq	1.98dq	1.85dq	5.55dq	5.59dq	1.92dq (7.5,1.5)	2.00dq (7,1.5)	2.25m
	1.89dq	1.89dq	1.83dq	1.84dd	1.87dd	1.74q(1.5)	1.92q(1.5)	2.1m
OCOCH$_3$	—	—	—	2.02s	1.94s	2.01s	1.75s	—

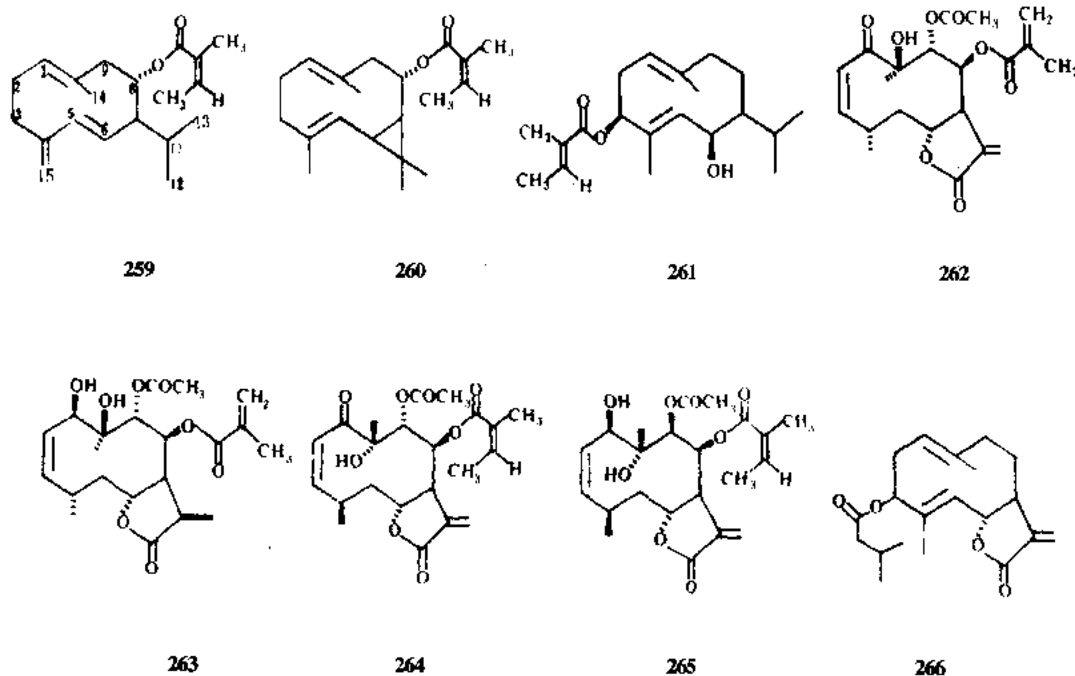
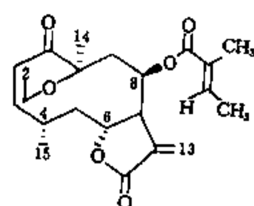
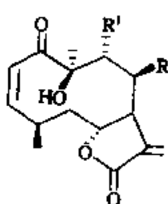


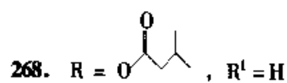
表 8-52　吉马烷衍生物 267～273 的 ^{1}H-NMR 化学位移[75]

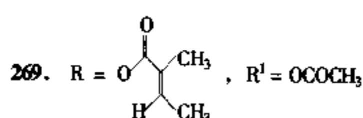
质子 \ 化合物	267	268	269	270	271	272	273
2-H	5.54bs	6.58d(12)	6.06d	6.60d	5.68	4.29d(4.5)	4.23d
3-H	—	5.88t(12)	5.08d	6.02t	—	3.33dd (9,4.5)	3.33dd
4-H	3.03q(7,1)	3.08tq (12,6)	2.80tq	3.12tq	—	1.47m	1.47m
5-H	2.59ddd (15,9,7)	1.81dt (12,5.5) 1.42dt (12,6)	1.26dt 1.00dt	1.84dt 1.44dt	6.23dt (4,1.5)	1.90m 1.48m	1.97m 1.47m
6-H	4.48bdd (9,5.0)	4.50dd (12,5.5)	4.48dd	4.58dd	5.31dt (4,1)	4.84dd (12,5.5)	4.80dd
7-H	3.30m (5,2.1)	2.61bs	2.48bs	2.64bs	3.75m	2.37bs	2.35bs
8-H	5.13ddd (5,2.5,1)	5.29ddd (11,6,3)	5.98dd	5.68dd	5.19ddd (5.5,3.5,1.5)	5.72bs (10,1.5)	5.66dd
9-H	2.70dd (15,5,5)	2.25dd (15,11)	5.73d	5.59d	2.54dd (14.5,5.5) 2.31dd (14.5,3.5)	5.89d(10)	5.76d
13-H_A	6.34d(3.5)	6.27bs(1)	6.17bs	6.33bs	6.34d(3.3)	6.32bs(1)	6.32bs
13-H_B	—	5.73d(1.5)	5.31bs	5.84bs	—	—	5.82bs
14-H	1.4s	1.44s	1.15	1.37s	1.49s	1.45s	1.47s
15-H	1.39d(7)	1.13d(6)	1.14d	1.14d	4.41bs	1.22d	1.22d

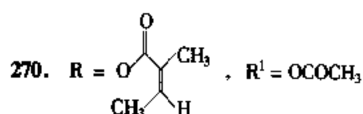


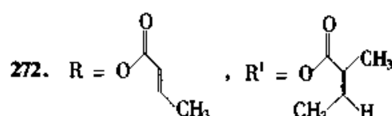
267

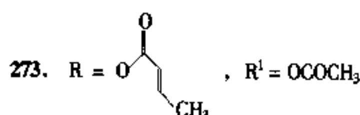


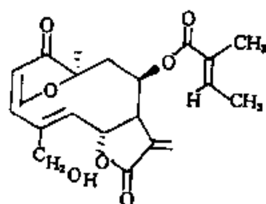












271

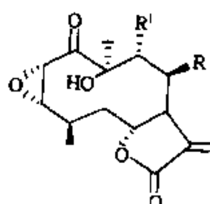
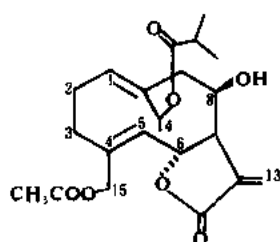
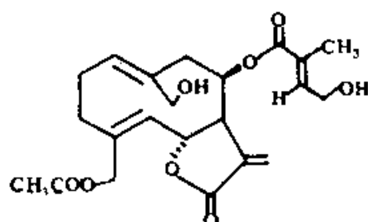


表 8-53 吉马烷衍生物 274～281 的 ^{1}H-NMR 化学位移[76]

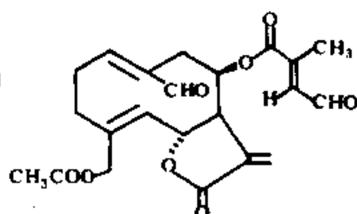
质子 \ 化合物	274	275	276	277	278	279	280	281
1-H	5.18dd (12,5)	5.21t(9)	6.43dd (13,4)	5.17m	5.18dd (12,6)	5.23dd (12,6)	5.32m	5.32m
2-H_A	1.63m	1.5～2.7m	—	—	—	—	—	—
2-H_B	2.40m	1.5～2.7m	—	—	—	—	—	—
3-H_A	2.40m	1.5～2.7m	—	—	—	—	—	—
3-H_B	2.64m	1.5～2.7m	—	—	—	—	—	—
5-H	5.04bs (10.5)	5.03bs(12)	5.30bs(10)	4.91d(10)	5.97d	5.75	5.50bs (11)	6.32d (10,5)
6-H	5.27dd (11,9)	5.14dd (10,9)	5.14m	5.40dd (9,10)	5.90	5.75	5.28dd (11,2.5)	5.44dd (10.5,2.5)
7-H	2.79m	2.97m	2.95m	2.74m	2.86m	2.89m	2.99m	3.14m
8-H	4.62m	5.81m	5.78m	4.58m	4.64m	5.80m	5.26ddd (1,2,4)	5.31m
9-H_A	2.22m	—	—	2.18m	2.18m	—	2.31dd (2,15)	—
9-H_B	2.96dd (15,6)	3.30dd (15,6)	3.60m	3.09m	3.09m	—	3.03m	—
13-H_A	5.62d(3)	5.65d(3)	5.64d(3)	5.58d(2.5)	5.97d(3)	5.64d(3)	5.74d(2)	5.70d(2)
13-H_B	6.38d(3.5)	6.33d(3.5)	6.32d(3.5)	6.30d(3)	6.43d(3.5)	6.32d(3.5)	6.31d(2.5)	6.47d(2)
14-H_A	4.56d(13)	3.76d(12)	9.89s	4.52d (12.5)	10.0s	4.03d (12.5)	4.5d (12.5)	4.54d(13)
14-H_B	4.73d(13)	4.16d(12)	—	4.69d (12.5)	—	4.72d (12.5)	4.82d (12.5)	4.87d(13)
15-H	4.51d(13)	4.57d(13)	4.51	4.01d(13)	4.16d (12.5)	8.72	4.08	9.46s
15-H_B	4.63d(13)	4.70d(13)	—	4.24d(13)	4.58d (12.5)	—	—	—
OCOR	1.18d(7) 1.11d(7)	6.74tq 4.28	5.66dq 10.15d(7)	2.38m 0.87t(7)	2.38m 1.51d(7) 1.70d(7)	2.34m 1.40d 1.64d	5.61bs 6.04bs	5.64bs 6.07bs



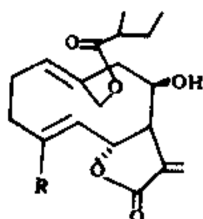
274



275



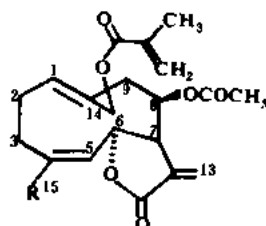
276



277. R = CH_2OH

278. R = CHO

279. R = CO_2H

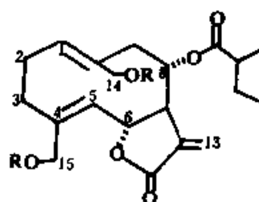


280. R = CH_2OH

281. R = CHO

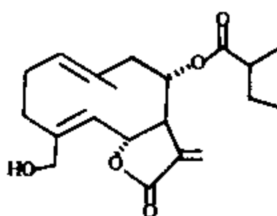
表 8-54 吉马烷衍生物 282 ~ 288 的 ^{1}H-NMR 化学位移[77,78]

化合物 / 质子	282	283	284	285	286	287	288
1-H	5.13m	4.70bd	4.67m	5.10m	5.82dd	5.65dd	5.62bd
2-H_α	2.1 ~ 2.6m	1.9 ~ 2.2m	1.95m	2.0 ~ 2.3m	5.01d	3.28m	3.34m
2-H_β	2.1 ~ 2.6m	1.9 ~ 2.2m	1.95m	2.0 ~ 2.3m	4.81d	2.3m	2.40m
3-H_α	2.1 ~ 2.6m	1.9 ~ 2.2m	2.36ddd	2.58bd	5.73s	2.0 ~ 2.3m	—
3-H_β	2.1 ~ 2.6m	1.9 ~ 2.2m	1.70m	2.0 ~ 2.3m	5.70s	2.0 ~ 2.3m	—
5-H	4.9bd	4.50bd	4.88bd	5.88d	3.03d	4.87bd	4.91bd
6-H	5.16dd	4.59dd	4.67dd	5.33dd	3.68dd	4.55dd	5.60dd
7-H	3.12dddd	2.58dddd	2.66dddd	3.08m	2.12m	2.52bdd	2.29m
8-H	5.35ddd	4.97ddd	4.97ddd	5.10m	5.23ddd	2.0m	1.85m
							2.3m
9-H_α	2.1 ~ 2.6m	2.68bd	2.48bd	2.0 ~ 2.3m	2.12m	2.13m	—
9-H_β	2.1 ~ 2.6m	2.07dd	2.15dd	2.0 ~ 2.3m	1.87dd	2.87bdd	2.81m
13-H_A	6.40dd	6.39dd	6.39dd	6.43bd	6.31d	6.21d	1.85m
13-H_B	5.96bd	5.63dd	5.73dd	5.96bd	5.58d	5.45d	1.45ddd
14-H_A	4.28bd	4.49bd	1.32bs	1.31bs	0.60s	—	—
14-H_B	3.93bd	4.24bd	—	—	—	—	—
15-H_A	4.37bd	4.39bs	3.88bd	10.01bs	9.16s	1.58d	1.68d
15-H_B	4.01bd	4.39bs	3.75bd	—	—	—	—
OCOR	2.39tq	2.15tq	2.21tq	2.38tq	2.20tq	—	—
	1.7m	1.70m	1.70m	1.75m	1.65m	—	—

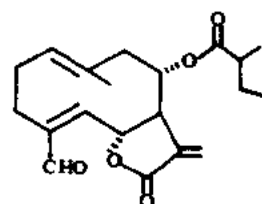


282. R = H

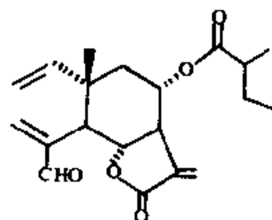
283. R = $COCH_3$



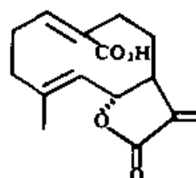
284



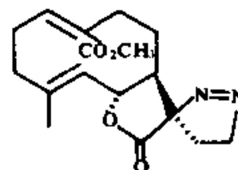
285



286



287



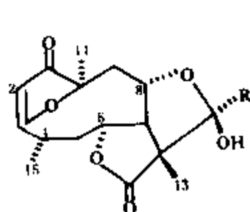
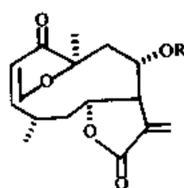
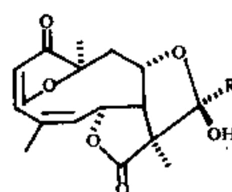
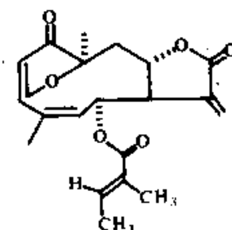
288

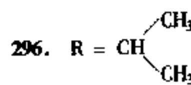
表 8-55 吉马烷衍生物 289 ~ 295 的^{1}H-NMR 化学位移[21]

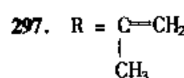
质子 \ 化合物	289	290	291	292	293	294	295
1-H	5.90dd	5.90dd	5.89dd	5.89dd	6.15dd	3.10dd	3.12dd
2-H_c	5.13bd	5.13bd	5.07bd	5.04bd	5.29d	2.63m	2.53dd
2-H_t	5.01bd	5.04bd	4.95bd	4.99bd	5.12d	2.63m	2.46dd
3-H_A	6.52bs	6.77bs	6.78bs	6.58bs	6.33d	6.63bs	6.77bs
3-H_B	6.16bs	6.21bs	6.19bs	6.21bs	5.62d	6.25d	6.21bs
5-H	3.75d	3.74d	3.74d	3.74d	3.47ddd	3.89d	3.88d
6-H	5.38dd	4.51m	5.04dd	5.04dd	4.91dd	5.45dd	4.59dd
7-H	3.41dddd	3.45m	3.32bdd	3.32bdd	3.56dddd	3.43dddd	3.45m
8-H	4.91dd	4.90dd	5.52dd	5.52dd	4.88dd	4.90dd	4.90dd
9-H	3.84dd	5.04m	4.38dd	4.38dd	3.95dd	4.05dd	5.03dd
13-H_A	6.34d	6.57d	6.60bs	6.38d	6.37d	6.31d	6.58d
13-H_B	5.81d	5.91d	5.89bs	5.83d	5.83d	5.74d	5.91d
14-H	1.33s	1.38s	1.43s	1.41s	0.98s	1.04s	1.08s
15-H	9.39s	9.31s	9.31s	9.39s	—	9.47s	9.36s
OCOR	6.29qq	6.15bs	6.24qq	6.22qq	3.13d	6.20qq	6.15bs

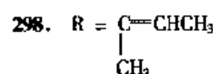
表 8-56　吉马烷衍生物 296～303 的 ^{1}H-NMR 化学位移[79]

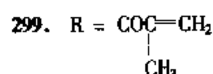
质子 \ 化合物	296	297	298	299	300	301	302	303
2-H	5.60d	5.61bs	5.61bs	5.70d	5.69d	5.65s	5.61s	5.71s
4-H	3.01dq	3.00dq	3.00dq	3.06dq	3.06dq	—	—	—
5-$H_α$	2.44ddd	2.44ddd	2.44ddd	2.49dd	2.49dq	6.04dq	6.03dq	6.00dq
5-$H_β$	2.15bd	2.15bd	2.15bd	2.11bd	2.11bd	—	—	—
6-H	4.22dd	4.24dd	4.24dd	4.34ddd	4.33ddd	5.02ddq	4.95ddq	5.28ddq
7-H	2.53dd	2.57dd	2.57dd	3.36bddd	3.36bddd	2.79dd	2.80dd	3.73dddd
8-H	3.91ddd	3.98ddd	3.99ddd	4.50dd	4.51dd	4.06ddd	4.04ddd	4.54ddd
9-$H_α$	2.01dd	2.01dd	2.02dd	2.35dd	2.34dd	2.00dd	2.00dd	2.47dd
9-$H_β$	2.34dd	2.46dd	2.44dd	2.48dd	2.48dd	2.48dd	2.32dd	2.30dd
13-H_A	1.35s	1.22s	1.17s	6.19d	6.16d	1.12s	1.33s	6.20d
13-H_B	—	—	—	5.46d	5.43d	—	—	5.44d
14-H	1.45s	1.45s	1.45s	1.49s	1.48s	1.43s	1.48s	1.53s
15-H	1.37d	1.38d	1.38d	1.42d	1.42d	2.07dd	2.07dd	2.08dd
OCOR	2.05qq	5.23bs	5.94bq	6.00dq	6.75qq	5.91q	2.05m	6.77qq
	1.08d	5.07bs	1.65dq	5.54dq	1.75dq	1.65bd	1.08d	1.77dq
	0.96d	1.90bs	1.77dq	1.83dd	1.71dq	1.77bs	0.99d	1.73dq
OH	2.22s	1.71s	2.53s	—	—	4.22s	2.80s	—

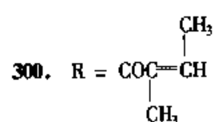





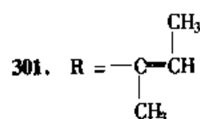












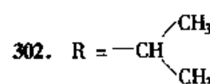
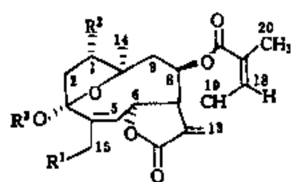
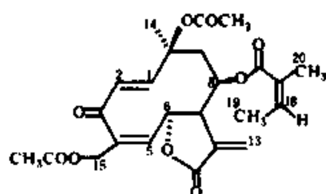


表 8-57　吉马烷衍生物 304～312 的 ^{1}H-NMR 化学位移[80]

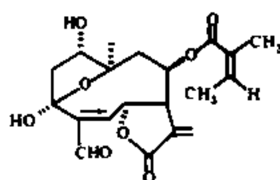
质子 \ 化合物	304	305	306	307	308	309	310	311	312
1-H	3.53t	4.08m	5.42bt	7.09d	—	—	4.16bt	4.02bt	7.39d
2-H	2.30d	—	2.65d	6.28d	—	—	—	2.50d	5.55d
5-H	5.62d	5.92bd	5.96bd	6.03bd	5.84bd	5.90dt	5.54bs	6.82d	5.82dd
6-H	5.14bt	5.44bt	5.18bt	5.42bdd	5.52bt	5.54dt	5.54m	5.55t	6.06dd
7-H	4.06m	4.30m	4.40m	3.38m	4.20m	4.20m	4.28m	4.47m	3.35m
8-H	5.60m	5.72m	5.68m	5.50m	5.66m	5.56m	5.74m	5.78m	5.54m
9-$H_α$	1.73dd	2.59dd	—	2.86dd	—	—	—	—	3.42dd
9-$H_β$	1.44dd	2.38dd	—	—	—	—	—	—	2.98dd
13-H_A	6.20d	6.31d	6.30d	6.41d	6.29d	6.31d	6.15d	6.37d	6.42d
13-H_B	5.37d	5.70d	5.64d	5.82d	5.66d	5.68d	5.77d	5.75d	5.88d
14-H	1.33s	1.57s	1.44s	1.72s	1.54s	1.54s	1.51s	1.62s	2.19s
15-H_A	3.91d	4.82bd	4.68bd	4.95bd	4.20bs	4.78bd	1.85bs	9.43s	4.90bs
15-H_B	3.75d	4.57bq	4.30bd	4.68bd	4.20bs	4.57bd			
18-H	5.88bq	6.10bq	6.08bq	6.13bq	6.07bq	6.09bq	6.08bq	6.11bq	6.10bq
19-H	1.91bd	1.92bd	1.91bd	1.96bd	1.93bd	1.95bd	1.73bd	1.93bd	1.97bd
20-H	1.75m	1.75m	1.75m	1.77m	1.87m	1.76m	1.73m	1.76m	1.83m
$COCH_3$	—	2.11s	2.04s	2.05s	—	2.10s	—	—	—
		—	2.07s	2.14s	—	—	—	—	—



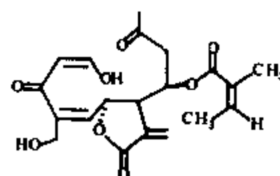
取代基 \ 化合物	304	305	306	308	309	310
R^1	OH	$OCOCH_3$	$OCOCH_3$	OH	$OCOCH_3$	H
R^2	OH	OH	$OCOCH_3$	H	H	OH
R^3	H	H	$COCH_3$	H	H	H



307



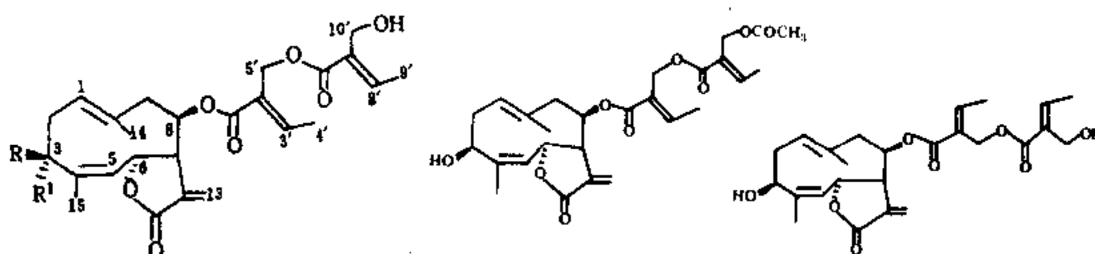
311



312

表 8-58 吉马烷衍生物 313～320 的 ^{1}H-NMR 化学位移[81～83]

质子 \ 化合物	313	314	315	316	317	318	319	320
1-H	5.25m	5.10bdd	5.09bdd	5.25m	5.29m	5.27m	5.27m	5.20m
2-H_α	2.3m	2.0m	2.0m	2.3m	2.67m	2.75m	2.75m	2.61m
2-H_β	2.75m	2.75m	2.75m	2.75m	2.79m	2.31m	2.3	—
3-H	5.25m	4.61dd	5.60dd	5.25m	4.47dd	5.27t	5.27m	5.26dd (4.5,3)
5-H	5.20dq	5.16bd	5.21bd	5.22dq	5.20dq	5.22dq (10,1.5)	5.20dq (10,1.5)	5.38bd (10.5)
6-H	5.90bd	5.23bd	5.27bd	5.27bd	6.30bd	5.96dd (10.5,2)	5.89dd (10.5,2)	5.68dd (10.5,2)
7-H	2.98bs	2.99bs	2.98bs	2.99bs	2.94bs	3.01m	2.99m	2.33bdd
8-H	5.27dd	5.29dd	5.29dd	5.30dd	5.29m	5.27m (4,3,1)	5.26m (4,3,1)	5.07m ($W_1/2$10)
9-H_α	2.45bd	2.42dd	2.40dd	2.45bd	2.41bd	2.77dd (15,3)	2.73dd (15,4)	—
9-H_β	2.75m	2.75m	2.75m	2.75m	2.67m	2.47dd (15,3)	2.45dd (15,2.8)	—
13-H_A	6.36d	6.37d	6.38d	6.37d	6.36d	6.36d(2)	6.35d (2.5)	}3.67
13-H_B	5.78d	5.77d	5.78d	5.78d	5.76d	5.81d(2)	5.78d(2)	
14-H	1.76bs	1.79bs	1.80bs	1.76bs	1.77bs	1.82bs	1.80bs	1.82bd (1,5)
15-H	1.83bs	1.79bs	1.88bs	1.84bs	1.72d	1.85d (1,5)	1.84d (1,5)	1.81d (1,5)
3'-H	7.10q	7.16q	7.11q	7.11q	7.20q	6.92t(6)	6.90t(6)	—
4'-H	1.93d	1.97d	1.98d	1.94d	1.95d	4.40d(6)	4.40d(6)	—
5'-H	4.94d 4.88d	4.89s	4.92s	4.93bs	4.85bs	4.33	4.34	—
8'-H	6.93q	6.98q	6.95q	7.10q	6.92q	—	—	—
9'-H	1.90d	1.93d	1.90d	1.94d	1.92d	—	—	—
10'-H	4.32bs	4.37bs	4.34s	4.48bs	4.40bd 4.33bd	— —	—	—



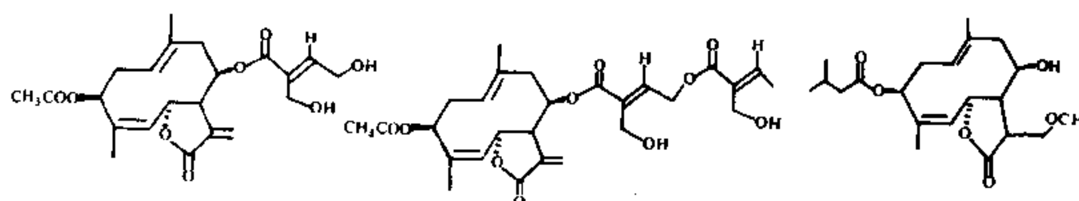
313. R = OCOCH$_3$, R^1 = H

314. R = H, R^1 = OH

315. R = H, R^1 = OCOCH$_3$

316

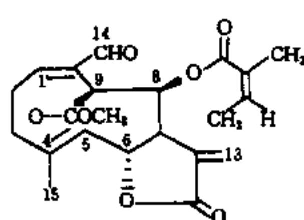
317



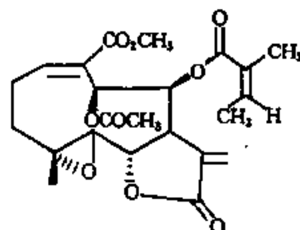
318　　319　　320

表 8-59　吉马烷衍生物 321 ~ 328 的^{1}H-NMR 化学位移[83~85]

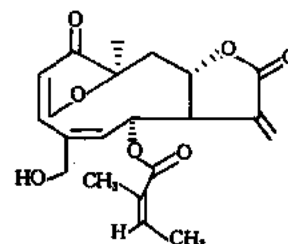
质子 \ 化合物	321	322	323	324	325	326	327	328
1-H	6.75dd	7.15dd	—	—	—	—	—	—
2-H	—	—	5.86s	5.83s	5.64s	5.68s	5.67s	5.62s
5-H	4.92bd	2.68d	6.32dt	6.27dt	5.98dq	5.98dq	5.99dq	5.99dq
6-H	5.09dd	4.29dd	5.48m	5.33dt	5.10ddq	5.03ddq	5.39ddq	5.23ddq
7-H	2.63m	2.99bd	3.85m	3.80m	3.66dddd	3.65dddd	3.63dddd	3.91dddd
8-H	6.81dd	6.74dd	4.58dt	4.53dt	5.20dd	5.07dd	5.51dd	5.07dd
	5.31dd	5.86d						
9-H$_\alpha$	—	—	2.30dd	2.30dd	4.19m	4.19m	5.32d	—
9-H$_\beta$	—	—	2.58dd	2.50dd	—	—	—	4.10dd
13-H$_A$	6.29d	6.36d	5.52d	5.49d	6.36d	6.37d	6.40d	6.36d
13-H$_B$	5.84d	5.93d	6.27d	6.22d	5.73d	5.70d	5.84d	6.05d
14-H	9.48d	—	1.55s	1.52s	1.68s	1.67s	1.52s	1.58s
15-H	2.01d	1.71s	4.43bs	4.38bs	2.07dd	2.06dd	2.08dd	2.06dd
OCOR	6.08qq	6.10qq	6.20m	6.02bs	7.10q	6.98q	7.11q	—
	1.95dq	1.95dq	1.90dq	1.83m	4.86d	4.27d	4.91d	—
	1.83dq	1.79dq	1.80m	—	4.71d	1.93d	4.66d	—
	—	—	—	—	1.97d	—	1.98d	—
OH	—	—	—	—	4.19m	4.08d	—	2.74d



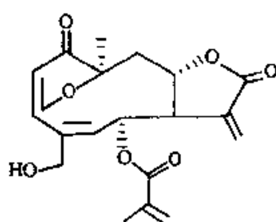
321



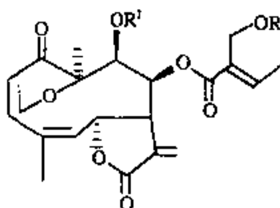
322



323



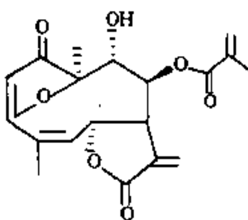
324



325. R = $COCH_3$, R^1 = H

326. R = R^1 = H

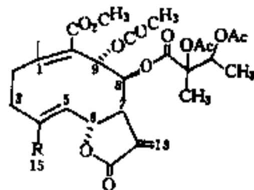
327. R = R^1 = $COCH_3$



328

表 8-60 吉马烷衍生物 329～336 的^{1}H-NMR 化学位移[86]

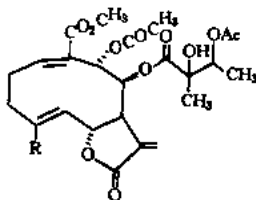
质子＼化合物	329	330	331	332	333	334	335	336
1-H	6.98dd (9.5,7.5)	7.00dd (9.5,7.5)	7.01dd (8.5,11.5)	7.00dd (10,7.5)	7.01dd (10,7.5)	7.02dd (10,7.5)	7.02dd (10,7.5)	7.02dd (10,7.5)
5-H	4.94d (8.5)	5.03d (10)	6.11d (10.5)	4.94d (10)	4.93d (10)	4.95d (10)	5.03d (10)	5.12d (10)
6-H	5.05dd	5.36dd (10,10.5)	5.77dd (10,10.5)	5.05	5.01	5.05	5.61dd (10,9.5)	5.28dd (10,10)
7-H	2.80m	2.80m	2.91m	2.83m	2.80m	2.83m	2.83m	2.80m
8-H	6.63dd (1.5,8)	6.62dd (1.5,8.0)	6.66dd (1,8)	6.71dd (1,8)	6.71dd (8.5,1.5)	6.68dd (8.5,1)	6.62dd (8.5,1)	6.71dd (8,1.5)
9-H	5.36d (8)	5.43d (8)	5.12d (8)	5.35 (8)	5.38d (8.5)	5.40d (8.5)	5.58d (8.5)	5.40d (8)
13-H_A	5.78d (3)	5.80d (3)	5.92d (3)	5.79d (3)	5.78d (3)	5.77d (3)	5.81d (3)	5.83d (3)
13-H_B	6.25d (3.5)	6.26d (3.5)	6.35d (3.5)	6.28 (3.5)	6.27d (3.5)	6.26d (3.5)	6.28d (3.5)	6.31d (3.5)
15-H	1.98bs	4.43d(14) 4.55d(14)	10.20	2.01	2.00	2.01	4.49	4.78d(13) 5.12d(13)
CO_2CH_3	3.78s	3.79s	3.79s	3.79	3.79	3.78	3.79	3.81
OCOR	5.16q (6.5)	5.51q (6.5)	5.23q (6.5)	5.06q (6.5)	5.06q (6.5)	5.06q (6.5)	5.18t (6.5)	5.08q (6.5)
	1.18d (6.5)	1.18d (6.5)	1.17d (6.5)	1.12d (6.5)	1.12d (6.5)	1.12d (6.5)	1.08d (6.5)	1.18d (6.5)
	1.53	1.57	1.52	1.27	1.27	1.27	1.27	1.32
$COCH_3$	2.01s	2.06s	1.99s	2.03s	2.04s	2.03s	1.96	1.96
	2.03s	2.06s	2.01s	—	1.97s	—	2.06	2.13
	2.04s	—	2.06s	—	—	—	—	—



329. R = CH_3

330. R = CH_2OH

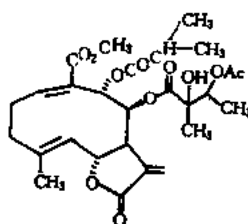
331. R = CHO



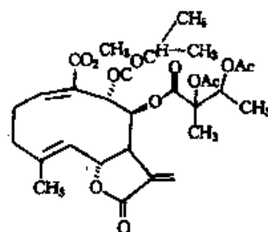
332. R = CH_3

333. R = CH_2OH

334. R = CH_2OCOCH_3



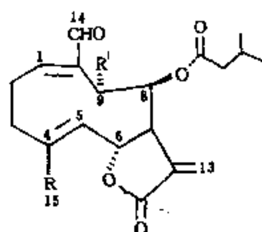
335



336

表 8-61 吉马烷衍生物 337 ~ 343 的^{1}H-NMR 化学位移[87]

质子 \ 化合物	337	338	339	340	341	342	343
1-H	6.64dd	6.67dd	5.78dd	6.81dd(9,7)	6.86dd	6.73dd	6.78dd
5-H	5.17bd	5.03bd	5.14bd	6.09bd(10)	6.26bd	4.91bd	5.02bd
6-H	5.24dd	5.24dd	5.34dd	5.82dd (10,10)	5.80dd	5.08dd	5.28dd
7-H	2.50bd	2.85bd	3.32bd	3.25bd (10,1.5)	3.11bd	2.61bd	2.64bd
8-H	6.38ddd	6.39dd	6.07dd	6.74dd (9,1.5)	6.40dd	6.72dd	6.69dd
9-H	2.80m 2.55m	4.12dd	5.46dd	5.05dd	2.85m 2.60m	5.25dd	5.34dd
13-H$_A$	6.25d	6.27d	6.24d	6.39d(3.5)	6.33d	6.30d	6.27d
13-H$_B$	5.60d	5.68d	5.64d	5.93d(3)	5.70d	5.80d	5.79d
14-H	9.47d	9.49d	4.50d	9.49d	9.48d	9.47d	9.51d
15-H$_A$	4.53dd	4.49dd	4.39bd (12.5)	10.23s	10.23s	2.01s	4.49d
15-H$_B$	4.31dd	4.32dd	4.21bd (12.5)				4.42d
OCOCH$_3$	—	—	1.97s	1.94s	—	1.96s	—

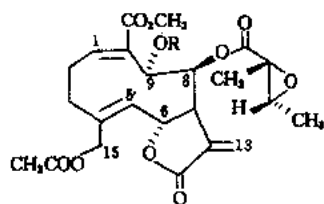


337 ~ 343

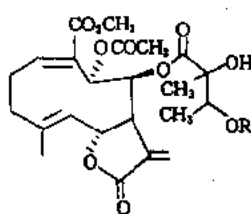
取代基 \ 化合物	337	338	339	340	341	342	343
R	CH$_2$OH	CH$_2$OH	CH$_2$OH	CHO	CHO	CH$_3$	CH$_2$OH
R^1	H	OH	OCOCH$_3$	OCOCH$_3$	H	OCOCH$_3$	OCOR

表 8-62 吉马烷衍生物 344 ~ 349 的^{1}H-NMR 化学位移[88,89]

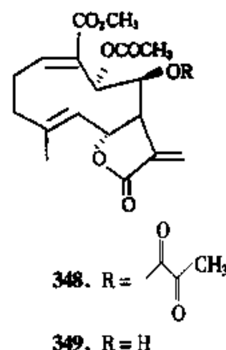
质子 \ 化合物	344	345	346	347	348	349
1-H	6.86bdd (10,7.5)	7.01bdd (10,7.5)	7.00dd (10,8)	7.00dd	7.02dd	7.00dd
2-H	2.0 ~ 3.0m	2.0 ~ 3.0m	—	—	—	—
3-H	2.0 ~ 3.0m	2.0 ~ 3.0m	—	—	—	—
5-H	5.07 ~ 5.33m	5.0 ~ 5.33m	4.93bs(10)	4.91bs	4.91bs	4.91bs
6-H	5.07 ~ 5.33m	5.0 ~ 5.33m	5.13t(10)	5.08t	5.17t	5.18t
7-H	2.52m	—	—	—	—	—
8-H	6.29dd (8.5,1.5)	6.66dd (8.5,1.5)	6.62dd (8.5,1.5)	6.62dd	6.65dd	6.58dd
9-H	4.11bs(9.8)	5.31d(8.5)	5.42d	5.36d	5.42d	5.35d
13-H$_A$	5.66d(3.5)	5.76d(3)	6.25d(3.5)	6.22d	6.25d	6.24d
13-H$_B$	6.22d(3.5)	6.28(3.5)	5.75d(3.2)	5.81d	5.73d	5.71d
OCH$_3$	—	—	3.80s	3.79s	3.80s	3.79s
15-H	4.79q	4.99q	1.98bs(1.2)	2.00bs	2.00bs	1.97bs
OCOR	3.02q(5.5)	3.02q	3.85q(6.5)	5.15q	—	—
	1.55s	1.44s	1.20s	1.23s	—	2.16bs
	1.26d(5.5)	1.12d(5.5)	1.16bs	1.22bs	—	1.48s
COCH$_3$	2.04s	2.00s	1.98s	1.91s	1.94s	1.97s



344. R = H
345. R = $COCH_3$



346. R = H
347. R = $COCH_3$

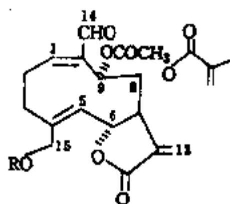


348. R =

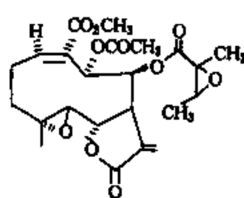
349. R = H

表 8-63 吉马烷衍生物 350 ~ 357 的^{1}H-NMR 化学位移[72,90,91]

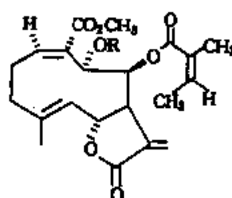
质子 \ 化合物	350	351	352	353	354	355	356	357
1-H	6.81dd (9,8)	6.74dd (9,8)	7.15dd (10,7)	7.00dd	6.84dd	—	—	—
2-H_α	2.81m	2.92m	2.3 ~ 2.5m	2.48m	2.30m	5.62s	5.73s	5.73s
2-H_β	2.69m	2.70m	2.3 ~ 2.5m	2.48m	2.30m	—	—	—
3-H	1.95m	1.95m	—	—	—	—	—	—
5-H	5.03d(10)	5.18d(10)	2.67d (9,5)	4.94d	4.94d	5.99dq	6.28bs	6.31bs
6-H	5.34t(10)	5.18d(10)	4.27dd (10,10)	5.11dd	5.09dd	5.23ddq	5.14bs	5.13bs
7-H	2.65m	2.70m	3.00m	2.79m	2.80m	3.91dddd	4.00bs	3.98bs
8-H	6.74dd (9,1)	6.70dd (9,1)	6.71dd (9,1)	6.67dd	6.33dd	5.07dd	4.91dd	4.90dd
9-H	5.44dd (9,2)	5.36dd (9,2)	5.87d(9)	5.40d	4.00dd	4.10dd	5.37d	5.37d
13-H_A	5.84d(3)	5.85d(3)	5.81d(3)	5.78d(3)	5.67d(3)	6.36t	6.30t	6.35t
13-H_B	6.26d(3)	6.28d(3)	6.30d(3)	6.25d(3)	6.24d(3)	6.05d	5.45d	5.46d
14-H	9.49d(2)	9.48d(2)	—	—	—	1.58s	1.44s	1.44s
15-H	4.51	4.87	1.70s	1.98bs	1.89bs	2.06dd	4.41bs	4.84ddd
OCOR	6.06bs	6.04bs	3.00m	6.05qq (7,1)	6.10qq	—	—	—
	5.60m	5.60m	1.43s	1.95dq (7,1)	1.98dq	—	—	—
	1.92bs	1.92bs	1.16d(5)	1.82qq (1,1)	1.89qq	—	—	—
$OCOCH_3$	1.95s	2.12s	2.03s	1.94s	—	—	—	—



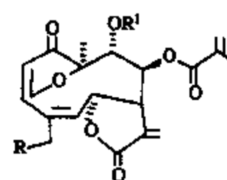
350. R = H
351. R = $COCH_3$



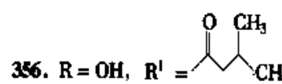
352



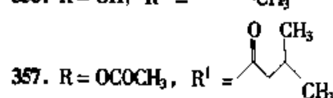
353. R = $COCH_3$
354. R = H



355. R = R^1 = H



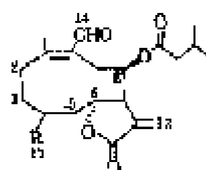
356. R = OH, R^1 =



357. R = $OCOCH_3$, R^1 =

表 8-64　吉马烷衍生物 358～363 的 ^{1}H-NMR 化学位移[87]

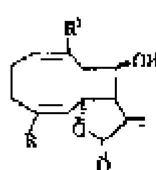
质子＼化合物	358	359	360	361	362	363
1-H	6.69dd(8)	6.53dd	6.63dd	5.35m	6.53dd	5.26dd
5-H	5.36bd(9)	6.43bd	5.56bd	5.47bd	6.45d	5.66dd
6-H	5.47dd(9,3)	5.64dd	5.46dd	5.17dd	5.63dd	5.58dd
7-H	2.66bs	2.76bs	2.66bs	2.45m	2.65bs	2.90bd
8-H	5.94ddd(2.5)	6.01ddd	5.95ddd	4.19ddd	4.85ddd	5.49ddd
13-H$_A$	6.34d(2)	6.44d	6.35d	5.20bs	6.50d	}1.12d
13-H$_B$	5.70d(2)	5.81d	5.72d	5.00bs	5.75d	
14-H	9.41d	9.38d	9.41d	3.89bs	9.36d	4.06bs
15-H	4.06bs	9.40s	4.53d	3.84bs	9.40s	3.97bs
			4.46d			



358. R = CH_2OH

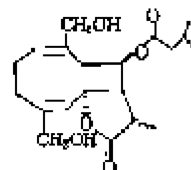
359. R = CHO

360. R = CH_2OCOCH_3



361. R = R^1 = CH_2OH

362. R = R^1 = CHO



363

表 8-65　吉马烷衍生物 364～369 的 ^{1}H-NMR 化学位移[92]

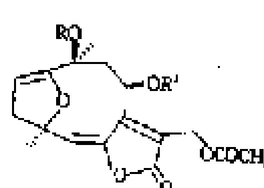
质子＼化合物	364	365	366	367	368	369
2-H	}2.5～2.0m	2.6～2.3m	2.5～2.1m	4.81dd	5.09dd	5.08dd
3-H				2.87dd	2.93dd	3.02dd
				2.71dd	2.82dd	2.92dd
5-H	5.93s	5.99s	6.06	5.88s	6.02s	6.02s
8-H	6.27bd	5.94dd	5.55dd	6.26bd	6.02dd	5.99dd
9-H$_α$	2.09dd	2.3m	2.5m	1.97dd	2.40dd	2.41dd
9-H$_β$	2.56dd	2.59dd	2.5m	2.64dd	2.72dd	2.72dd
13-H$_A$	5.09d	5.05d	5.05d	5.02s	5.07s	5.08d
13-H$_B$	4.97d	4.92d	4.86d	5.02s	4.87s	4.86d
14-H	1.59s	1.63s	1.54s	1.66s	1.64s	1.65s
15-H	1.25s	1.63s	1.36s	1.40s	1.63s	1.63s
$OCOCH_3$	2.07s	2.08s	2.11s	2.08s	2.12s	2.12s
	2.06s	2.04	—	—	2.03s	2.03s
OCH_3	—	—	3.28s	—	—	—
$OCOCH_2$	—	—	2.38dq	2.38dq	2.35dq	—
CH_3			1.16t	1.16t	1.14t	



364. R = $OCOCH_3$, R^1 = H

365. R = $OCOCH_3$, R^1 = $COCH_3$

366. R = $OCOCH_2CH_3$, R^1 = CH_3



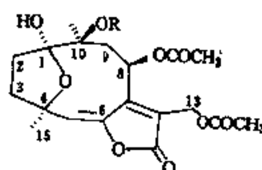
367. R = H, R^1 = $COCH_2CH_3$

368. R = $COCH_3$, R^1 = $COCH_2CH_3$

369. R = $COCH_3$, R^1 = $COCH_3$

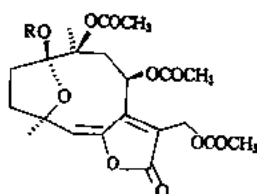
表 8-66 吉马烷衍生物 370 ~ 376 的^{1}H-NMR 化学位移[93,94]

质子＼化合物	370	371	372	373	374	375	376
1-H	—	—	—	—	—	5.14bt	6.43bt
2-H	2.1 ~ 2.3m	1.9 ~ 2.2m	2.40m	2.1 ~ 2.3m	5.07dd	2.18dt	2.66dt
3-H					3.02dd	2.12t	2.28t
5-H	5.61s	5.67s	5.71s	5.70s	6.01s	4.92dd	5.00dd
6-H	—	—	—	—	—	1.92d	1.90d
7-H	—	—	—	—	—	5.17d	5.07d
8-H	5.61s	6.16bd	5.62dd	5.97dd	5.98dd	5.62dt	5.57dt
9-H$_\alpha$	2.2m	2.11m	2.19dd	2.2m	2.40dd	2.69d	2.84d
9-H$_\beta$	2.52dd	2.35dd	2.83dd	2.66bd	2.70dd	2.69d	2.84d
12-H	—	—	—	—	—	1.07s	1.05s
13-H$_A$	5.03d	5.11d	5.05d	5.05d	5.07d	1.07s	1.05s
13-H$_B$	4.87d	5.04d	4.88d	4.90d	4.85d	—	—
14-H	1.16s	1.36s	1.31s	1.52s	1.64s	4.12s	10.02s
15-H	1.12s	1.12s	1.24s	1.39s	1.62s	1.43dd	1.43dd
OCOCH$_3$	1.70s	1.74s	1.73s	1.82s	2.12s	—	—
	1.68s	1.65s	1.73s	1.69s	2.07s	—	—
	1.64s	—	1.57s	1.60s	2.02s	—	—
OCH$_3$	—	—	3.28s	—	—	—	—



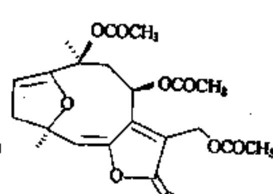
370. R = COCH$_3$

371. R = H

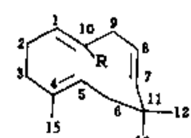


372. R = CH$_3$

373. R = H



374

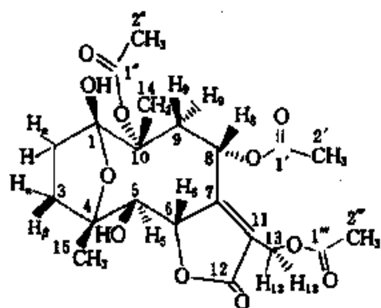


375. R = CH$_2$OH

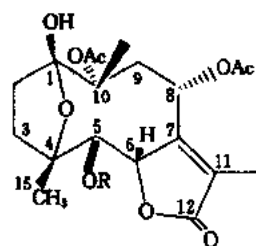
376. R = CHO

表 8-67 吉马烷衍生物 377 ~ 379 的^{1}H-NMR 化学位移[127]

质子＼化合物	377	378	379	质子＼化合物	377	378	379
2-H	2.11m	2.2m	2.2m	9β-H	2.57dd		2.53d
2β-H	2.15m	2.2m	2.2m		(12,3)		(4)
3-H	2.11m	2.2m	2.2m	9α-H			
3β-H	1.81m	1.8m	1.8m	13-H	4.89d	1.91br	1.90s
5-H	3.52d	3.49d	4.85d		(16)		
	(9)	(9)	(9)	13'-H	4.72d		
6-H	5.08d	4.96d	5.05d		(16)		
	(9)	(9)	(9)	14-H	1.60s	1.61s	1.61s
8-H	5.87t	5.81dd	5.86d,d	15-H	1.48s	1.48s	
	(3)	(8,4)	(8,4)	OAc	2.02,2.05,2.08	2.00,2.06	2.11,2.05,2.01



377



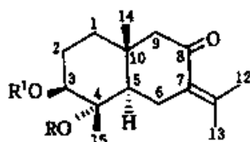
378. R = H

379. R = Ac

八、桉叶烷衍生物类化合物的¹H-NMR 化学位移

表 8-68 桉叶烷衍生物 380 ~ 385 的¹H-NMR 化学位移[95]

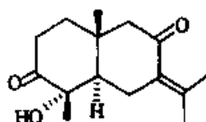
质子＼化合物	380	381	382	383	384	385
1-H_α	—	—	1.44ddd	1.65ddd	—	—
1-H_β	—	—	—	1.91ddd	—	—
2-H_α	—	—	2.30m	2.80ddd	—	—
2-H_β	—	—	1.74m	2.47ddd	—	—
3-H	5.95dd	4.81dd	3.53dd	—	6.04dd	4.87dd
5-H	—	—	—	2.00dd	4.05d	2.63d
6-H_α	3.19dd	3.06dd	2.97dd	2.97bdd	7.10d	7.25d
6-H_β	—	—	—	2.42dd	—	—
9-H_α	2.23d	2.19d	2.17d	2.17bd	2.29d	2.31s
9-H_β	2.28d	2.25d	2.24d	2.30d	2.36d	—
12-H	2.01d	2.02d	2.03d	2.06d	1.46s	1.50s
13-H	1.80bs	1.84d	1.84d	1.87d	1.51d	1.51d
14-H	0.99s	0.98s	0.95s	1.19s	1.00s	0.99s
15-H	1.41s	1.25s	1.20s	1.36s	1.40s	1.26s
OCOR	6.08qq	6.12qq	—	—	6.09qq	6.15qq
	1.99dq	2.01dq	—	—	2.00dq	2.02dq
	1.92dq	2.92dq	—	—	1.92dq	1.93dq



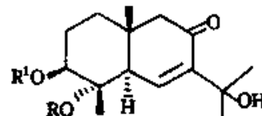
380. R = $COCH_3$，R^1 = 当归酰基

381. R = H，R^1 = 当归酰基

382. R = R^1 = H



383



384. R = $COCH_3$，R^1 = 当归酰基

385. R = H，R^1 = 当归酰基

表 8-69 桉叶烷衍生物 386 ~ 393 的¹H-NMR 化学位移[95~98]

质子＼化合物	386	387	388	389	390	391	392	393
1-H	4.77dd	4.87dd	—	—	1.68ddd	1.69ddd	7.14bs	4.92bs
2-H_α	2.02m	2.0m	—	—	0.95m	0.92m	—	—
2-H_β	2.33m	2.48m	—	—	0.95m	0.92m	—	—
3-H	5.34m	5.33m	2.32bd	5.75bs	2.00m	2.00ddd	7.39bs	6.97bs
5-H	2.21bs	2.0m	1.98bs	2.12bs	3.01dd	3.01dd	—	—
6-H_α	5.76bs	2.0m	5.38bs	5.38bs	2.92dd	2.95dd	—	—
6-H_β	—	—	—	—	2.37ddt	2.39ddt	5.22d	5.29d
7-H	—	—	—	—	—	—	2.25ddd	1.9 ~ 2.2m
8-H_α	—	—	—	—	—	—	2.16dddd	1.9 ~ 2.2m
8-H_β	—	—	—	—	—	—	1.96m	1.9 ~ 2.2m
9-H_α	—	5.32dd	—	—	6.42s	6.45s	2.85ddd	2.79ddd
9-H_β	—	—	—	—	—	—	3.15bdd	3.09bdd
12-H	1.03d	1.00d	1.04d	1.04d	—	—	1.89bs	1.88bs
13-H	0.86d	0.92d	0.87d	0.87d	4.49bs	4.87d	4.99dq	4.97bs
14-H	1.18s	1.03s	1.07s	1.14s	0.92s	0.82s	—	—
15-H_A	1.68bs	1.68bs	4.74bs	1.67bs	4.80ddd	4.81ddd	—	—
15-H_B	—	—	4.60bs	—	5.07ddd	5.08ddd	—	—
$OCOCH_3$	2.07s	2.06s	—	—	—	2.09s	2.33s	—

386

387

388

389

390. R = CH_2OH

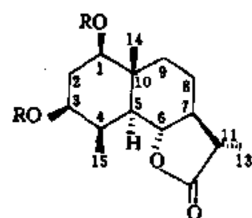
391. R = CH_2OCOCH_3

392. R = H

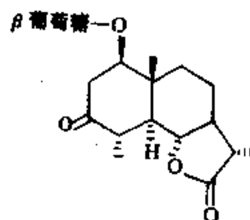
393. R = $COCH_3$

表 8-70 桉叶烷衍生物 394～399 的 ^{1}H-NMR 化学位移[63,77,99]

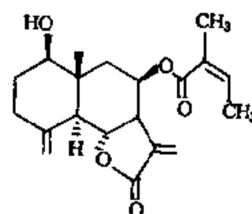
质子 \ 化合物	394	395	396	397	398	399
1-H	3.35ddd	4.58dd	3.64dd	3.54dd	5.55dd	3.60d
2-H_α	1.80m	1.93m	2.76dd	1.93m	5.84dd	—
2-H_β	1.80m	1.93m	2.41dd	1.64m	—	—
3-H_α	3.78dddd	4.82ddd	—	2.15ddd	5.75bs	—
3-H_β	—	—	—	2.37ddd	—	—
4-H	2.29ddq	2.58ddq	2.51dq	—	—	—
5-H	1.44dd	1.59dd	1.38dd	2.28bd	2.71bd	—
6-H	4.20dd	3.94dd	3.96dd	4.52dd	4.20dd	4.65bd
7-H	1.57dd	1.59bdd	1.51m	2.87dddd	2.84dddd	—
8-H_α	1.80m	1.70m	1.91bd	5.84ddd	5.23ddd	5.39bt
8-H_β	1.57	1.44dddd	—	—	—	—
9-H	1.8～1.9	1.67～1.86	2.19bd	2.41dd	—	—
				1.64m		
11-H	2.47dq	2.34dq	2.27dq	—	—	—
13-H	1.15d	1.22d	1.23d	6.18d	6.15d	1.24d
				5.50d	5.54d	
14-H	1.03s	1.12s	1.08s	0.98s	0.99s	1.20s
15-H	0.98d	1.00d	1.24d	5.04bs	2.00s	1.82bs
				4.96bs		
O—C(=O)—R	—	—	—	6.11qq	—	—
	—	—	—	1.93dq	—	—
	—	—	—	1.86dq	—	—



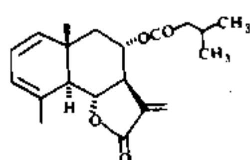
394. R = H
395. R = $COCH_3$



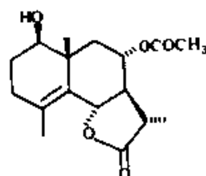
396



397



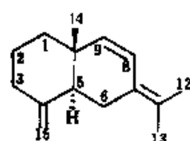
398



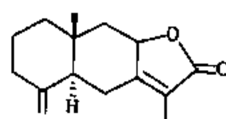
399

表 8-71 桉叶烷衍生物 400 ~ 407 的 ^{1}H-NMR 化学位移[100]

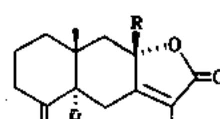
质子 \ 化合物	400	401	402	403	404	405	406	407
3-H	2.49d	2.65m	2.35m	2.37bd	2.36m	2.39bd	2.39bd	2.36bd
5-H	1.95 ~ 2.23m	2.01m	2.00m	2.00m	2.03m	2.0 ~ 2.2	—	—
6-H_α	1.95 ~ 2.23m	2.67dd	2.74dd	2.63dd	2.68dd	2.0 ~ 2.2	2.69dd	—
6-H_β	1.95 ~ 2.23m	2.26dd	2.30dd	2.44dd	2.36m	2.0 ~ 2.2	2.50m	—
8-H	6.31d	5.05dd	4.84dd	—	—	—	—	—
9-H_α	5.4d	2.38m	2.35m	1.56d	1.43d	2.0 ~ 2.2	5.60s	2.33d
9-H_β	5.4d	2.38m	2.35m	2.27d	2.79d	2.0 ~ 2.2	—	2.20d
12-H	1.79bs	—	—	—	—	3.15m	—	—
13-H	1.77bs	1.84dd	1.83dd	1.82d	1.87d	1.34d	1.91d	1.24d
14-H	0.80s	0.69s	0.90s	1.03s	0.94s	0.80s	0.95s	0.71s
15-H_A	4.81ddd	4.91ddd	4.88ddd	4.87ddd	4.88ddd	4.84ddd	4.92ddd	4.83ddd
15-H_B	4.59ddd	4.66ddd	4.61ddd	4.60ddd	4.60ddd	4.60ddd	4.63ddd	4.51ddd



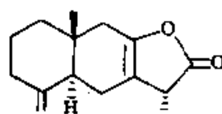
400



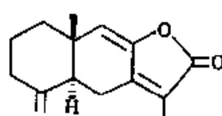
401



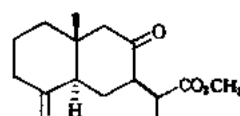
402. R = H
403. R = OH
404. R = $OCOCH_3$



405



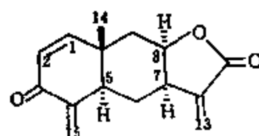
406



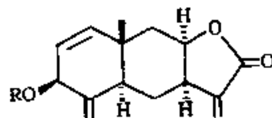
407

表 8-72 桉叶烷衍生物 408~415 的^{1}H-NMR 化学位移[101~103]

质子 \ 化合物	408	409	410	411	412	413	414	415
1-H	6.82d(10)	5.53dd (9.5,2.2)	5.42dd (10,2)	—	—	4.87dd	3.77dd	5.93d
2-H	6.00d(10)	5.60dd (9.5,2.5)	5.70dd (10,2)	—	—	1.8m	1.73m	5.86d
3-H	—	4.68bdd (2.5,2)	5.88bdd (2.5,2)	—	4.00bdd (12,3.5)	2.12m	2.14m	2.97d
5-H	2.61dd (14,25)	2.17dd (14,2.5)	2.28dd (14,2.5)	2.25dd (14,2.5)	—	—	—	1.77dd
6-H_{α}	2.03ddd (14,7,2.5)	1.82ddd (14,7,2.5)	1.82ddd (14,7,2.5)	1.98ddd (14,7,2.5)	—	5.97d	5.87d	2.09ddd
6-H_{β}	1.54q(14)	1.55q(14)	1.54q(14)	1.39q(14)	—	—	—	1.47ddd
7-H	3.09m	3.04m	3.03m	3.02m	—	3.41dddd	3.44dddd	2.99ddd
8-H	4.50ddd (5,4.5,2)	4.53ddd (5,4.5,2)	4.50ddd (5,4.5,2)	4.55ddd (5,4.5,2)	4.48ddd (5,4.5,2)	4.83ddd	4.85ddd	4.47ddd
9-H_{α}	2.39dd (15,2)	2.28dd (15,2)	2.25dd (15,2)	2.33dd (15,2)	2.20dd (15,2)	1.95dd	1.89dd	1.56dd
9-H_{β}	1.80dd (15,4.5)	1.64dd (15,4.5)	1.65dd (15,4.5)	1.57dd (15,4.5)	1.45dd (15,4.5)	2.08dd	2.56dd	2.23dd
13-H_A	6.19d(1)	6.16d(1)	6.16d(1)	6.18d(1)	—	6.35d	6.33d	6.30d
13-H_B	5.69d(1)	5.63d(1)	5.55d(1)	5.60d(1)	1.23d(7)	5.84d	5.85d	5.64d
14-H	1.04s	0.92s	0.97s	0.99s	0.80s	1.22s	1.10s	1.12s
15-H_A	6.11bs	5.27bs	5.00bs	5.90dd (2,1)	5.16bs	1.71bs	1.65bs	1.34s
15-H_B	5.20bs	4.73bs	4.68bs	5.02dd (2,1)	4.65bs	—	—	—
O—C(=O)—R	—	—	—	—	—	6.89qq	6.88qq	—
	—	—	—	—	—	1.84dq	1.82dq	—
	—	—	—	—	—	1.87dq	1.86dq	—

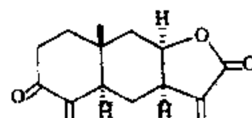


408

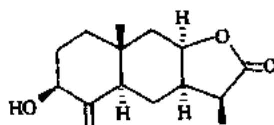


409. R = H

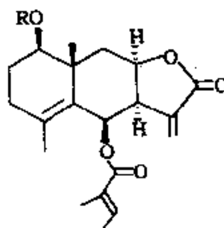
410. R = $COCH_3$



411

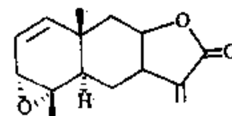


412



413. R = $COCH_3$

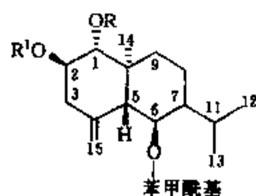
414. R = H

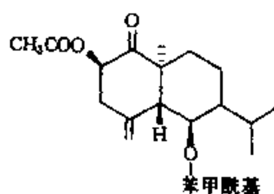


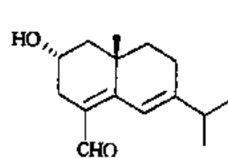
415

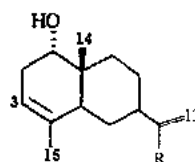
表 8-73　桉叶烷衍生物 416～422 的^{1}H-NMR 化学位移[78,104,105]

质子 \ 化合物	416	417	418	419	420	421	422
1-H	3.47d	5.23d	—	3.26d	(α)1.37dd (β)1.83ddd	3.55dd	3.58dd
2-$H_α$	4.82ddd	5.29ddd	5.51dd	3.63ddd	—	2.0m	2.02m
2-$H_β$	2.69dd	2.70dd	2.88dd	2.60dd	4.15dddd	2.3m	2.33m
3-H	2.16bdd	2.17bdd	2.50bdd	2.12bdd	(α)2.02dd (β)2.96dd	5.29bs	5.30bs
5-H	2.54bd	2.63bd	2.68bd	2.53bd	—	—	—
6-H	5.46dd	5.67dd	5.54dd	5.44dd	6.92bs	1.91ddd	1.93
7-H	2.05dddd	2.12m	2.0m	2.03m	—	2.53ddd	2.54
8-$H_α$	1.75m	1.45m	1.8～1.95m	1.75m	2.32m	—	—
8-$H_β$	1.75m	1.45m	1.8～1.95m	1.75m	2.19ddd	—	—
9-$H_α$	1.85bd	1.63bd	1.90bd	1.85bd	1.62dd	—	—
9-$H_β$	1.41ddd	1.26m	1.45m	1.36ddd	1.72ddd	—	—
11-H	2.07m	1.94dqq	2.0m	2.05m	2.41qq	—	—
12-H	0.96d	1.00d	0.94d	0.94d	1.11d	4.16bs	9.55
13-H	0.94d	0.80d	0.91d	0.92d	1.11d	5.07dt 4.95bs	6.30s 6.00s
14-H	0.93s	0.88s	1.22s	0.87s	1.13s	0.79s	0.81s
15-H_A	4.94bs	4.80bs	5.18bs	4.88bs	10.34s	1.60bs	1.58bs
15-H_B	4.48bs	4.67bs	4.74bs	4.42bs	—	—	—
$OCOCH_3$	2.10s —	1.80s 1.76s	2.18s —	— —	— —	— —	— —









416. R = H，$R^1 = COCH_3$
417. $R = R^1 = COCH_3$
418. $R = R^1 = H$

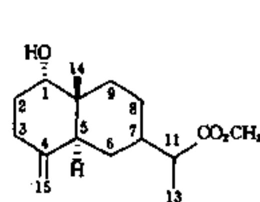
419

420

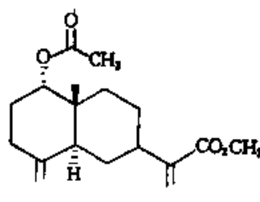
421. $R = CH_2OH$
422. R = CHO

表 8-74　桉叶烷衍生物 423～428 的^{1}H-NMR 化学位移[106,107]

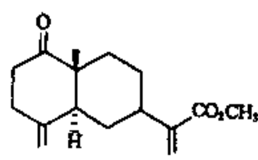
质子 \ 化合物	423	424	425	426	427	428
1-H	3.44dd	4.82dd	—	3.47dd	1.2 1.7	1.2 1.8
2-$H_α$	1.83ddd	1.9m	2.21ddd	1.90ddd	1.8	1.8
2-$H_β$	1.94ddd	1.9m	2.35ddd	1.99ddd	1.8	1.8
3-$H_α$	2.40bddd	2.35m	2.05bddd	2.41bdd	3.6	3.6
3-$H_β$	2.12dd	2.20ddd	2.15ddd	2.13ddd	3.6	3.6
5-H	2.32bd	2.43bd	1.93bd	2.43bd	2.7	2.0
6-$H_α$	—	—	1.79ddd	—	7.1	2.9
6-$H_β$	1.33ddd	1.34ddd	1.37ddd	1.33ddd	—	2.0
7-H	1.83m	2.51dddd	2.51dddd	2.55dddd	—	—
8-$H_α$	1.7m	1.75m	1.65dddd	1.73m	—	—
8-$H_β$	1.49ddd	1.45ddd	1.29dddd	1.45dddd	—	—
9-H	1.70m	1.75m	(α)1.76ddd (β)1.96ddd	1.73m	2.30	2.21
11-H	2.34dq	—	—	—	—	—
13-H_A	1.15d	6.16bs	6.23d	6.16bs	1.45	2.03
13-H_B	—	5.59bs	5.29dd	5.58bs	—	1.84
14-H	0.71s	0.86s	0.80d	0.76s	0.98	0.94
15-H_A	4.74ddd	4.79ddd	4.78ddd	4.76ddd	1.22	1.22
15-H_B	4.44ddd	4.49ddd	4.58ddd	4.45ddd	—	—
OCH_3	3.68s	3.77s	3.42s	3.76s	—	—



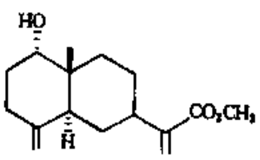
423



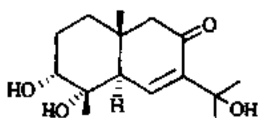
424



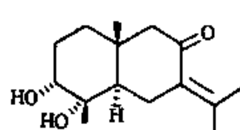
425



426



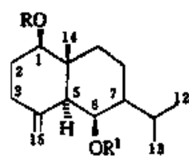
427

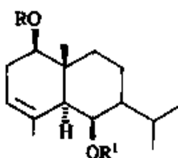


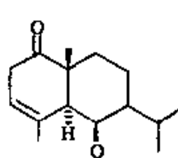
428

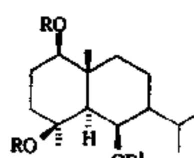
表 8-75 桉叶烷衍生物 429 ~ 436 的^{1}H-NMR 化学位移[108]

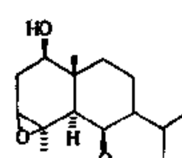
质子 \ 化合物	429	430	431	432	433	434	435	436
1-H	3.39dd	4.66dd	5.53d	4.77dd	—	3.30bdd	4.57dd	3.34dd
2-H	1.60m	—	2.27bd	—	3.09bd	—	—	2.38dd
			1.98bdd		2.71bd			
3-H	2.33bd	2.35bs	5.33bs	5.33bs	5.51bs	—	2.62ddd	2.99bd
	2.18m	2.20m						
5-H	1.93bs	2.03bs	2.09bs	2.21bs	2.44bs	1.42d	1.84d	1.78d
6-H	5.77bs	5.78bs	5.74bdd	5.75bdd	5.81bs	5.89bdd	6.03bs	5.83bs
9-H	2.06ddd	—	2.00dd	—	—	—	—	1.90ddd
			1.19m					
11-H	1.35dqq	—	1.47dqq	1.45dqq	1.45dqq	—	—	1.40dqq
12-H	1.06d	1.05d	1.05d	1.04d	1.06d	0.92d	1.00d	1.08d
13-H	0.87d	0.87d	0.88d	0.87d	0.89d	0.91d	0.87d	0.88d
14-H	1.03s	1.12s	1.10s	1.19s	1.39s	1.17s	1.36s	1.11s
15-H	4.80bs	4.82bs	1.19bs	1.69bs	1.77bs	1.21s	1.51s	1.28s
	4.66bs	4.72bs						
OCOR	7.70d	7.70d	7.67d	7.67d	7.70d	7.73d	7.70d	7.73d
	6.41d	6.41d	6.38d	6.38d	6.42d	6.47d	6.44d	6.44d
	7.54m	7.54d	7.57m	7.52m	7.54m	7.56m	7.55m	7.55m
	7.39m	7.38d	7.38m	7.38m	7.40m	7.46m	7.40m	7.40m
$OCOCH_3$	—	2.08s	—	2.08s	—	—	2.06s	—
	—	—	—	—	—	—	2.05s	—









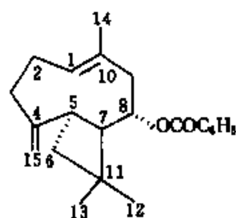


429. R = H, R^1 = 肉桂酰基
430. R = $COCH_3$, R^1 = 肉桂酰基
431. R = H, R^1 = 肉桂酰基
432. R = $COCH_3$, R^1 = 肉桂酰基
433
434. R = H, R^1 = 肉桂酰基
435. R = $COCH_3$, R^1 = 肉桂酰基
436

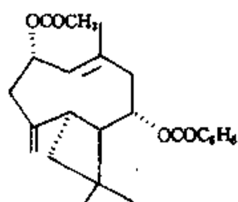
九、石竹烷衍生物类化合物的^{1}H-NMR 化学位移

表 8-76 石竹烷衍生物 437 ~ 446 的^{1}H-NMR 化学位移[109 ~ 111]

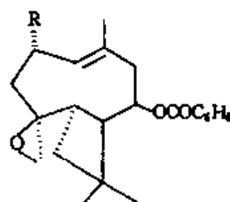
质子 \ 化合物	437	438	439	440	441	442	443	444	445	446
1-H	5.50bdd	5.39bd	5.60bdd	5.40bdq	5.13bdq	2.67m	2.48ddd	2.56ddd	2.55ddd	2.13m
2-H	—	5.58ddd	—	5.61ddd	4.66ddd	—	—	—	—	1.55m
3-H	—	—	—	—	—	2.24m	—	1.99ddd	1.39m	1.95m
						2.09m		2.22m	1.96m	
4-H	—	—	—	—	—	2.31m		2.36m	1.75m	—
5-H	2.50ddd	2.49ddd	2.37m	2.54m	2.54ddd	5.88m	6.22dd	6.19ddd	2.34ddd	5.30m
6-H	1.7m	1.65m	1.6m	1.52dd	1.52dd	—	—	—	—	2.13m
				1.21dd	1.21dd					
7-H$_\alpha$	}2.26dd	2.05m	2.09m	1.84dd	1.84dd	2.31m	2.1m	3.17ddd	2.81bd	}2.28m
7-H$_\beta$						2.24m	2.95dd	2.78m	3.36dd	
8-H	5.22ddd	5.30ddd	5.22ddd	5.37ddd	5.36ddd	1.59m	4.06m	4.40bd	5.37dd	—
9-H$_\alpha$	2.12dd	2.08m	2.16dd	1.70dd	1.68dd	1.95m	1.93dd	2.35d	2.00dd	}2.65dd
9-H$_\beta$	2.70dd	2.87dd	2.70dd	3.27ddd	3.27ddd	—	—	—	—	
10-H$_\alpha$	—	—	—	—	—	1.70dd	1.48dd	1.43dd	1.62dd	}3.86d
10-H$_\beta$	—	—	—	—	—	1.75dd	1.58dd	1.86dd	1.75dd	
12-H$_A$	}1.19s	1.19s	1.10s	1.10s	1.10s	5.06d	4.97bs	}5.16s	5.04bs	}1.00s
12-H$_B$						4.85d	4.82bs		4.93bs	
13-H	1.00s	1.00s	0.96s	1.00s	1.00s	1.04s	1.22s	1.14s	1.07s	0.98s
14-H	1.76bs	1.74bs	1.83bs	1.82bs	1.80bs	0.98s	1.14s	1.09s	0.99s	1.59bs
15-H$_A$	5.07bs	5.14bs	}2.76d	2.77dd	2.76dd	—	—	—	—	5.02d
15-H$_B$	4.94bs	5.11bs		2.73d	2.69d	—	—	—	—	4.89



437



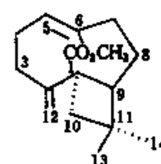
438



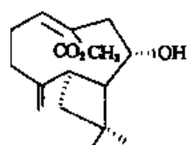
439. R = H

440. R = OCOCH$_3$

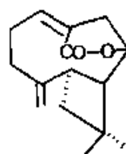
441. R = OH



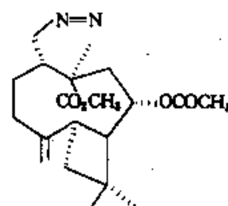
442



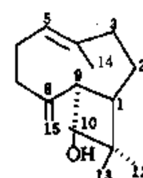
443



444



445

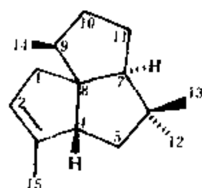


446

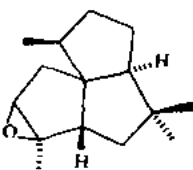
十、其他三环倍半萜类化合物的^{1}H-NMR 化学位移

表 8-77 三环倍半萜类化合物 447 ~ 453 的^{1}H-NMR 化学位移[112-114]

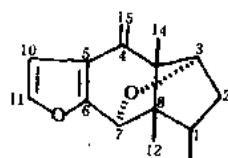
质子 \ 化合物	447	448	449	450	451	452	453
1-H_A	2.55bd	1.57bd	—	—	1.7 ~ 2.4m	2.25ddq	—
1-H_B	2.48bd	1.40bd	—	—	—	—	—
2-H_A	}5.13bs	3.16bs	—	—	—	1.84dd	—
2-H_B			—	—	—	2.79ddq	—
3-H	—	—	3.90m	—	5.36s	—	2.09ddd
4-H	2.32m	1.88m	—	—	2.36q	—	—
5-H	2.32m	1.96m	—	—	1.7 ~ 2.4m	—	—
6-H	—	—	—	—	—	5.08q	—
7-H	1.78dd	1.70dd	4.20m	4.30bd	4.27bs	—	—
9-H	1.98dq	2.05dq	—	—	—	—	—
10-H	1.66m 1.20dd	1.18dd	6.36bd(2)	6.36bd(2)	6.10d(8)	—	—
11-H	1.66m	—	7.20d(2)	7.27d(2)	9.90d(8)	—	—
12-H	1.08s	1.11s	0.95s	1.07s	1.23s	0.88d	1.01s
13-H	1.17s	1.19s	1.10d(8)	0.87d(9)	1.07d(7)	1.10s	1.98q
14-H	0.84s	1.07d	1.30s	1.25s	1.30s	1.54d	1.68q
15-H_A	1.60ddd	1.32s	4.95s	5.05s	1.30d	1.18s	1.01d
15-H_B	—	—	5.10s	5.16s	—	—	—



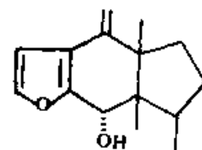
447



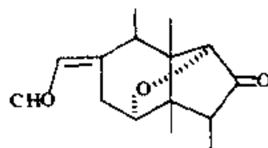
448



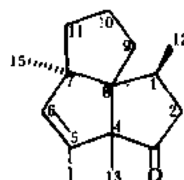
449



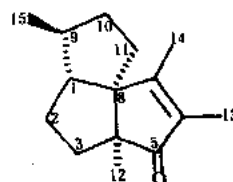
450



451



452



453

表 8-78 三环倍半萜类化合物 454 ~ 462 的^{1}H-NMR 化学位移[115]

质子 \ 化合物	454	455	456	457	458	459	460	461	462
1-H	5.58ddd	4.02bd	3.57bdd	3.46dd	4.15dd	4.14bd	—	—	—
2-H	5.44ddd	4.12ddd	3.30bd	3.38d	—	—	—	—	—
3-H_A	2.46ddd	2.06d	2.09d	1.90d	—	—	—	—	—
3-H_B	2.16ddd	1.87dd	1.42dd	2.09dd	—	—	—	—	—
5-H_A	1.69d	}1.60m	1.94d	}1.49s	1.57dd	1.62dd	1.95bd	4.94bs	4.91bs
5-H_B	1.63d		1.46d				2.22bd	—	—
7-H	1.88dd	2.76dd	2.56dd	1.94dd	2.32dd	—	—	2.26bq	2.60bq
9-H	2.00ddq	2.12ddq	1.96ddq	2.07ddq	2.16ddq	2.15ddq	1.72ddq	1.67m	1.67m
11-H	—	—	—	—	—	—	—	1.82m	
12-H	1.08s	1.06s	1.09s	1.05s	1.07s	1.21s	1.00s	0.97s	0.93s
13-H	0.93s	0.96s	0.96s	0.92s	0.96s	0.96s	1.52bs	1.62dd	1.56dd
14-H	0.98s	0.98s	0.96s	1.00s	0.94s	0.92s	1.55bs	0.98d	0.99d
15-H	0.82d	0.99d	0.96d	1.16d	1.00d	1.25d	0.96d	0.94d	0.96d

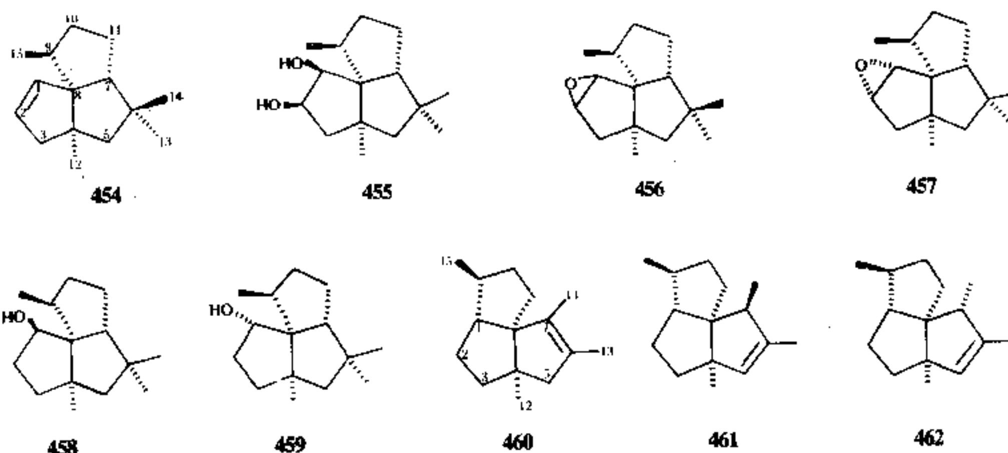
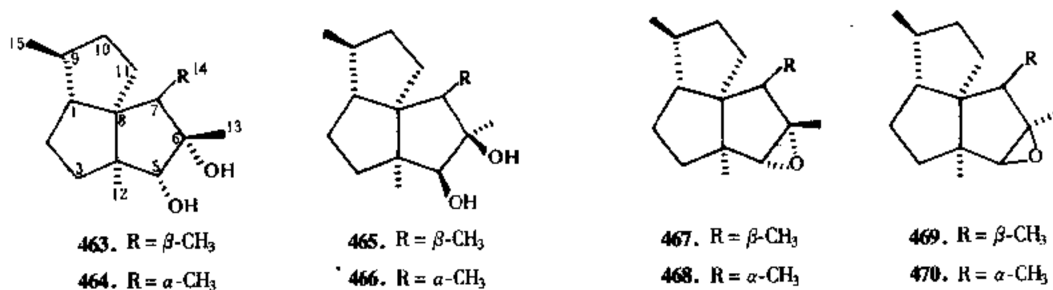


表 8-79　三环倍半萜类化合物 463～470 的^{1}H-NMR 化学位移[115]

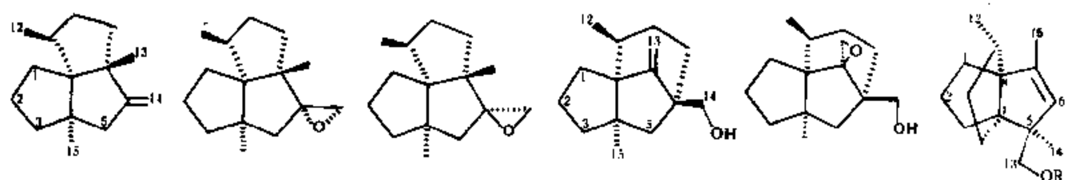
质子 \ 化合物	463	464	465	466	467	468	469	470
5-H	3.26d	3.34s	3.33s	3.34d	2.94s	2.97s	2.95s	2.97s
7-H	1.89q	1.57q	1.55m	2.01q	1.93q	2.07q	—	1.88q
11-H	2.18m	1.97m	—	—	1.93m	1.93m	—	—
12-H	1.04s	1.01s	0.97s	0.94s	1.08s	1.06s	0.94s	0.90s
13-H	1.10s	1.18s	1.17s	1.13s	1.33s	1.31s	1.38s	1.29s
14-H	0.91d	0.99d	0.94d	0.98d	1.03s	0.97d	0.98d	1.04d
15-H	0.93d	0.96d	0.93d	0.99d	0.91d	0.95d	0.92d	0.95d
OH	2.44bs	2.39bs	2.13d	2.48d 2.11s	—	—	—	—



463. R = β-CH$_3$　464. R = α-CH$_3$
465. R = β-CH$_3$　466. R = α-CH$_3$
467. R = β-CH$_3$　468. R = α-CH$_3$
469. R = β-CH$_3$　470. R = α-CH$_3$

表 8-80　三环倍半萜类化合物 471～478 的^{1}H-NMR 化学位移[116,117]

质子 \ 化合物	471	472	473	474	475	476	477	478
1-H	—	—	—	—	—	2.02bd	2.16bd	1.95bd
3-H	—	—	—	—	—	1.81ddd	—	1.82ddd
5-H$_A$	2.35ddd	1.56d	1.37d	1.41d	1.34d	—	—	—
5-H$_B$	2.10bd	1.97d	2.13d	1.82d	2.33d	—	—	—
6-H	—	—	—	—	—	4.78q	4.82q	4.75q
9-H	2.00ddq	2.10ddq	2.03dd	2.01ddq	2.0m	—	—	—
12-H	0.92d	0.93d	0.93d	0.81d	0.89d	0.91d	0.99d	0.92d
13-H$_A$	}1.10s	0.84s	0.75s	4.74s	2.98d	4.04d	3.58d	4.23d
13-H$_B$						3.99d	3.42d	4.17d
14-H$_A$	4.65ddd	2.83dd	2.67d	3.72d	3.43d	}1.05s	1.05s	1.07s
14-H$_B$	4.62ddd	2.64d	2.59d	4.62s	2.81d			
15-H	0.99s	1.06s	1.02s	1.08s	1.13s	1.55d	1.62d	1.54d



471　472　473　474　475

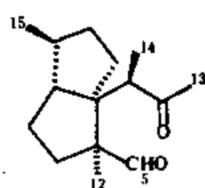
476. R = $COCH_3$

477. R = H

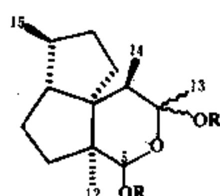
478. R = $COC_6H_3(NO_2)_2$

表 8-81　三环倍半萜类化合物 479～488 的 ^{1}H-NMR 化学位移[115]

质子 \ 化合物	479	480	481	482	483	484	485	486	487	488
5-H	9.65s	4.26s	4.68s	4.40s	4.30s	4.76d	4.60s	4.61d	4.36s	3.46s
12-H	1.15s	1.00s	1.07s	0.89s	0.96s	0.98s	1.08s	0.94s	0.98s	1.03s
13-H	2.09s	1.34s	1.33s	1.33s	1.75q	1.75q	2.24s	2.26s	4.00d	5.04s 4.91s
14-H	1.23d	0.97d	0.97d	0.99d	1.59q	1.60q	1.35s	1.45s	1.70s	1.26s
15-H	1.03d	0.94d	0.95d	1.01d	1.03d	1.04d	0.90d	1.02d	1.03d	0.97d

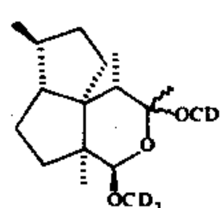


479

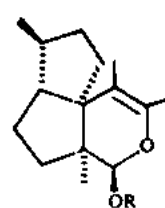


480. R = CD_3

481. R = D

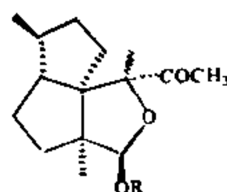


482



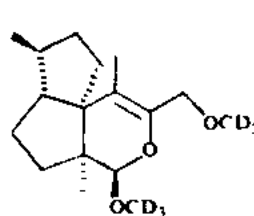
483. R = CD_3

484. R = H

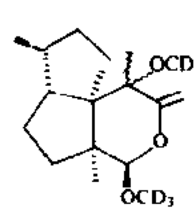


485. R = CD_3

486. R = H



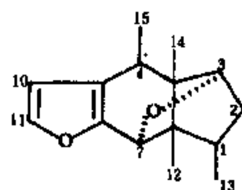
487



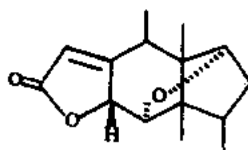
488

表 8-82　三环倍半萜类化合物 489～496 的^{1}H-NMR 化学位移[88,118]

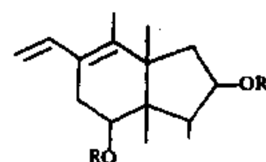
质子＼化合物	489	490	491	492	493	494	495	496
1-H	1.9m	—	1.95m	—	2.95q(7)	—	—	—
2-H	2.3m	—	3.78m	4.70ddd (7,7,4)	—	—	—	4.56ddd
3-H	3.96bs ($W_{1/2}=7$)	4.06bs	—	—	2.15d(18) 2.90d(18)	—	2.52m	2.25m
4-H	2.60q(8)	2.77q(8)	—	—	—	2.54q(7)	1.2m	—
6-H	—	4.22d(2)	2.65dd (15,6)	2.26dd (16,6)	3.15bs	—	1.92m	1.95m
7-H	4.38s	3.91s	3.78m	5.01m	—	2.22dd 2.15d	5.57bdd	5.48bdd
9-H	—	—	—	—	—	—	2.40m	—
10-H$_A$	6.29bd (2)	5.57(2)	6.71dd (15,9)	6.73dd (18,12)	6.80dd (17,12)	6.16d(3)	5.13bd	5.02bs
10-H$_B$							4.79bs	4.83bs
11-H	7.34d(2)	—	5.01d(9) 5.15d(15)	5.05d(12) 5.13d(18)	5.15d(17) 5.18d(1)	7.20bs ($W_{1/2}=3.5$)	2.31m	—
12-H	1.22s	1.25s	0.95s	0.88s	1.01s	0.73s	0.98d	0.93d
13-H	1.16d(8)	1.00d(8)	1.13d(8)	1.08d(7)	0.91d(7)	0.85d(7)	0.78d	0.75d
14-H	1.10s	1.05s	0.97s	1.04s	1.16s	0.82s	5.10dq	5.29dq
15-H	1.16d(8)	1.03d(8)	1.80bs	1.77bs	1.91bs	1.12d(7)	1.22d	1.51d
OCOCH$_3$	—	—	—	1.98s	—	—	2.11s	2.09s
	—	—	—	2.07s	—	—	—	—



489

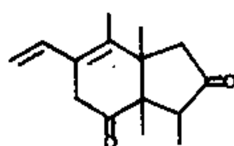


490

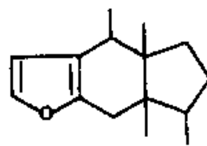


491. R = H

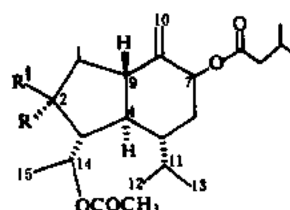
492. R = COCH$_3$



493



494

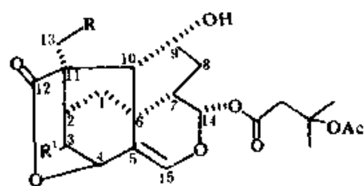


495. R^1 + R = O

496. R^1 = OCOCH$_3$
R = H

表 8-83 三环倍半萜类化合物 497～505 的 ^{1}H-NMR 化学位移[8,119,120]

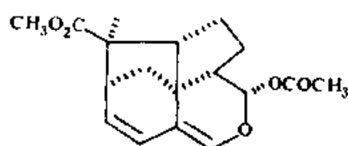
质子 \ 化合物	497	498	499	500	501	502	503	504	505
1-Hα	1.42dd	1.45dd	1.37dd	1.85m	2.19m	2.28m	2.35m	2.45m	2.45m
1-Hβ	3.05ddd	3.18dd	3.07ddd	2.09m	2.45dd	2.38dd	—	2.30m	—
2-H	2.38bdd	2.40m	2.38bdd	2.64bdd	—	4.62ddd	5.58ddq	5.40ddq	5.28ddq
3-Hα	1.90m	4.97dd	1.87m	}5.81m			—	—	—
3-Hβ	2.13dddd	—	2.13m		2.65dd	—	—	—	—
4-H	4.87ddd	4.88dd	4.83ddd	5.81m	1.50ddd	—	—	—	—
5-H	—	—	—	—	1.90m	—	2.14bdq	2.15bdq	2.30bdq
6-Hα	—	—	—	—	5.15m	5.04dd	1.22dd	1.28dd	1.25m
6-Hβ	—	—	—	—	—	—	1.77m	1.89m	2.03m
7-Hα	}2.53ddd	2.60ddd	2.54ddd	2.06dd	5.81d	5.76d	1.45dddd	1.48dddd	2.03m
7-Hβ					—	—	1.60dddd	1.65dddd	1.70m
8-Hα	2.2m	2.2m	2.2m	2.09m	—	—	1.81dd	1.83dd	2.18dd
8-Hβ	1.9m	1.9m	1.9m	1.8m	—	—	—	—	—
9-H	4.48ddd	4.42dd	4.41ddd	1.8m 1.44m	2.15m	—	—	—	—
10-H	2.2m	2.2m	2.2m	2.87dd	5.30bs 4.94d	5.23bs 4.98d	2.35m	2.30m	2.61dd
11-H	—	—	—	—	—	—	3.50bs	4.77bs	—
12-H	—	—	—		2.82d 2.68d	2.76d 2.72d	1.14s	1.18s	1.15s
13-H	1.60s	4.74d 4.61d	1.59s	1.29s	1.23s	1.20s	1.07s	1.03s	1.11s
14-H	5.42d	5.46d	5.42d	6.01d	5.24m	5.15m	0.89d	0.86s	0.92d
15-H	6.47s	6.53s	6.43s	6.09s	1.25d	1.56d	1.68ddd	1.51ddd	1.82ddd



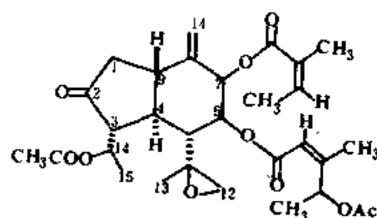
497. R = H, R^1 = OCOCH$_3$

498. R = OCOCH$_3$, R^1 = H

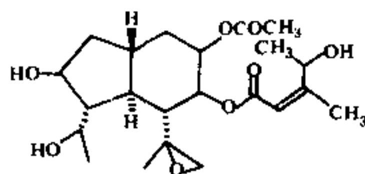
499. R = R^1 = H



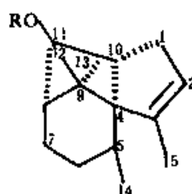
500



501

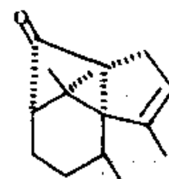


502



503. R = H

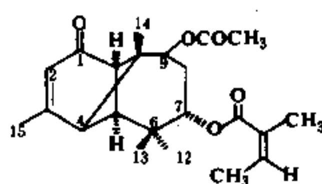
504. R = OCCH$_3$



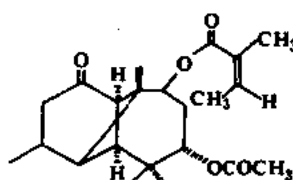
505

表 8-84 三环倍半萜类化合物 506 ~ 514 的 ^{1}H-NMR 化学位移[32,36,121,122]

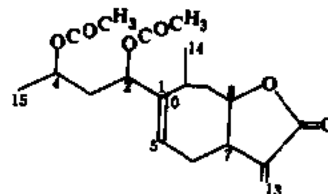
质子 \ 化合物	506	507	508	509	510	511	512	513	514
1-H	—	—	—	—	—	1.43bs	1.48bs	1.37bs	2.16bdd 1.86bd
2-H	5.80bs	2.20m 2.58dd	5.10dd	—	5.22dd	1.49bd 1.07bd	1.53bd 1.06bd	1.57bd 0.91bd	5.25bs
3-H	—	—	—	—	—	0.87s	0.85s	0.85s	—
4-H	2.68bd	2.20m	4.88ddq	3.80ddq	4.88ddq	—	—	—	2.34bd 2.03m
5-H	2.32	2.20m	5.83bdd	5.58bdd	5.87bdd	—	—	—	0.66dd
6-H	—	—	—	—	—	—	—	—	0.78dd
7-H	5.13dd	4.88dd	3.23m	2.55m	2.52m	1.63bd 1.12bd	1.63bd 1.12bd	1.57bd 0.96bd	—
8-H	—	—	4.63ddd	4.26ddd	4.38ddd	1.35m	1.35m	1.35m	—
9-H	5.12dd	5.03dd	—	—	—	1.90m	1.90m	1.97m	2.03m
10-H	—	—	—	—	—	5.92tq	6.96tq	6.94tq	5.12bt
11-H	3.11d	3.06d	—	—	—	—	—	—	—
12-H	0.99s	0.95s	—	—	—	9.39s	—	—	1.59bs
13-H$_A$ 13-H$_B$	}0.89s	0.89s	6.28d 5.53d	6.16d 5.44d	6.17d 5.45d	}1.71bs	1.92bs	1.89bs	1.67bs
14-H	1.07s	1.03s	1.14d	1.14d	1.11d	1.00s	0.99s	1.11s	1.02s
15-H	2.05d	1.12d	1.24d	1.22d	1.25d	0.76s	0.79s	—	1.59bs



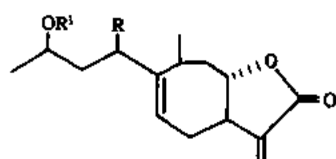
506



507



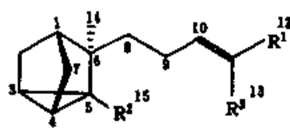
508



509. R = R^1 = H

510. R = OCOCH$_3$,

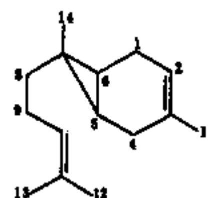
R^1 = COCH$_3$



511. R^1 = R^2 = CH$_3$, R^3 = CHO

512. R^2 = R^3 = CH$_3$, R^1 = CO$_2$CH$_3$

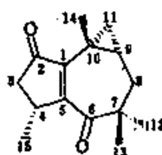
513. R^1 = R^2 = CO$_2$CH$_3$, R^3 = CH$_3$



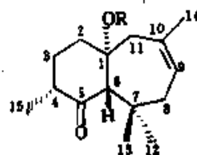
514

表 8-85　三环倍半萜类化合物 515～517 的 ^{1}H-NMR 化学位移[128]

质子 \ 化合物 \ 溶剂	515		516		517
	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	$CDCl_3$
2α-H	—	—	1.39～1.54m	1.91brdd	3.00brdd
2β-H	—	—	1.39～1.54m	1.74m	1.95m
3α-H	1.63dd	2.06dd	1.39～1.54m	1.74m	1.39m
3β-H	2.18dd	2.71dd	1.69～1.81m	1.88dddd	2.00dddd
4-H	3.07ddq	3.35ddq	1.89m	2.37brddq	2.42brddq
6-H	—	—	2.01brs	2.45brs	2.41brs
8α-H	0.94brdd	1.24brdd	1.59dd	1.77dd	1.86brdd
8β-H	1.60dd	2.02dd	1.91brdd	2.11brdd	2.11brdd
9-H	0.68dddd	1.06dddd	5.54tsext.	5.71tsext.	5.68m
11α-H	0.39t	0.51t	1.86dd	2.13dd	3.09dd
11β-H	0.77dd	0.95dd	2.45brdd	2.80brdd	2.85brdd
12-Me	0.88s	1.06s	1.49s	1.35s	1.29s
13-Me	1.21s	1.35s	1.03s	0.98s	1.00s
14-Me	1.14s	1.20s	1.67td	1.80td	1.75td
15-Me	0.66d	1.04d	1.02d	0.99d	1.00d



515

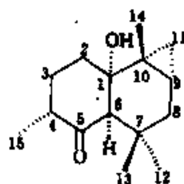


516. R = H

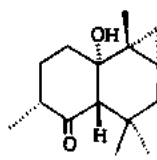
517. R = CONHCOCCl$_3$

表 8-86　三环倍半萜类化合物 518～520 的 ^{1}H-NMR 化学位移[129]

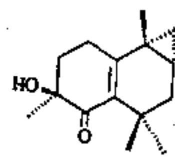
质子 \ 化合物 \ 溶剂	518		519		520	
	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
2α-H			1.96～2.08m	1.48～1.70m	2.25ddd	1.71～1.99m
2β-H	2.31, 1.84m	1.90, 1.68m	1.96～2.08m	1.72ddd	2.76ddd	2.25m
3α-H	1.96, 1.47m	1.47, 1.14m	1.79m	1.48～1.70m	2.14ddd	1.71～1.99m
3β-H			1.96～2.08m	1.48～1.70m	1.92m	1.71～1.99m
4-H	2.39m	1.93m	2.38dddq	1.92dddq	—	—
6-H	2.39d	2.08d	2.32brs	1.71brs	—	—
8α-H	2.06brdd	2.39brdd	1.56～1.74m	1.59dd	1.17m	1.01brdd
8β-H	1.59ddd	1.59ddd	1.56～1.74m	1.47brdd	1.92m	1.73dd
9-H	0.86dddd	0.73dddd	0.92m	0.65dddd	1.13m	0.79dddd
11α-H	−0.09t	0.04t	1.00t	0.87t	0.25t	−0.04t
11β-H	0.46dd	0.30dd	0.24dd	−0.03dd	0.91dd	0.56dd
12-Me	1.00s	1.13s	0.94brs	1.08brs	1.09s	1.23s
13-Me	1.11brs	1.10brs	1.28s	1.28s	1.26brs	1.33brs
14-Me	1.09brs	0.92brs	1.14brs	1.14brs	1.24brs	0.86brs
15-Me	1.00d	0.95d	1.01d	1.08d	1.24d	1.15brs
O-H	1.55brs	0.41brs	—	0.57brs	4.12brs	4.34brs



518



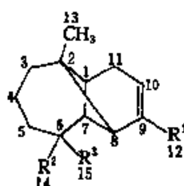
519



520

表 8-87　三环倍半萜类化合物 521～525 的^{1}H-NMR 化学位移[130]

质子＼化合物	521	522	523	524	525
1-H	1.96～2.15m	2.17d(6.0)	2.05～2.15m	2.01～2.17m	2.08～2.17m
3-H	1.49～1.64m	1.55～1.72m	1.50～1.65m	1.48～1.71m	1.50～1.73m
5a-H	1.28～1.38m	1.43～1.52m	1.33～1.42m	1.28～1.37m	1.28～1.37m
5b-H	1.96～2.15m	2.00～2.11m	2.05～2.15m	2.01～2.17m	2.08～2.17m
7-H	1.96～2.15m	2.06s	2.03s	2.01～2.17m	2.15s
8-H	1.96～2.15m	2.17d(6.0)	2.30～2.36m	2.01～2.17m	2.28d(6.3)
10-H	5.18～5.22m	5.18～5.21m	5.18～5.22m	5.16～5.19m	5.49～5.51m
11-H	2.23～2.27m	2.22～2.25m	2.30～2.36	2.20～2.24m	2.31～2.34m
12-H	1.67q(2.0)	1.66q(2.0)	3.99q(1.52)	1.64q(2.0)	3.75～3.78m
13-H	0.82s	0.84s	0.83s	0.80s	0.83s
14-H	1.07s	3.53d(6.40)	1.08s	3.26s	1.08
COOMe	3.64s	3.69s	3.65s	3.65s	3.64s
CH_2OMe	—	—	—	3.22s	3.27s



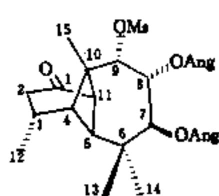
	R^1	R^2	R^3
521.	CH_3	CH_3	COOMe
522.	CH_3	CH_2OH	COOMe
523.	CH_2OH	CH_3	COOMe
524.	CH_3	CH_2OMe	COOMe
525.	CH_2OMe	CH_3	COOMe

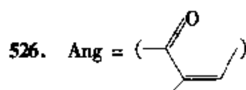
表 8-88　三环倍半萜类化合物 526～534 的^{1}H-NMR 化学位移[131]

质子＼化合物	526	527	528	529	530
1-H	—	—	—	—	—
2α-H	2.16(dd,19,6)	2.03(dd,16,4)	2.05(dd,16,4)	2.14(dq,16,1)	2.10(dd,17,3)
2β-H	2.62(dd,19,9)	2.44(dd,16,7)	2.45(dd,16,8)	2.79(dd,16,7)	2.46(dd,17,8)
3-H	2.39(m)	2.18(m)	2.17(m)	2.41(m)	2.28(m)
4-H	2.36(brd,6)	1.92(m)	2.01(m)	2.01(m)	2.02(m)
5-H	1.87(brs)	2.09(dd,6,4)	2.19(dd,5,3)	2.21(dd,6,3)	2.17(dd,6,3)
7-H	5.46(d,11)	3.36(s)	3.63(s)	5.01(s)	4.54(s)
8-H	5.51(dd,11,2)	—	—	—	—
9-H	5.02(d,2)	5.44(五重峰,1)	5.44(五重峰,1)	5.66(五重峰,1)	5.48(五重峰,1)
11-H	3.03(d,6)	2.78(brd,6)	2.62(brd,5)	3.01(brd,5)	2.80(brd,6)
12-CH_3	1.13(d,7)	1.07(d,7)	1.09(d,7)	1.06(d,7)	1.10(d,7)
13-CH_3	1.12(s)	1.04(s)	1.13(s)	0.97(s)	0.96(s)
14-CH_3	0.97(s)	1.05(s)	0.94(s)	1.19(s)	1.17(s)
15-CH_3	1.11(s)	1.65(d,1)	1.72(d,1)	1.77(d,1)	1.74(d,1)

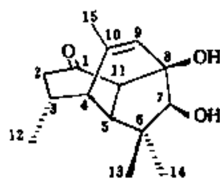
续表

质子 \ 化合物	531	532	533	534
1-H	—	—	—	5.14(m)
2α-H	2.12(dq,15,1)	2.06(dd,16,5)	2.17(qd,16,1)	1.78～1.86(m)
2β-H	2.98(dd,15,7)	2.46(dd,16,8)	2.74(dd,16,8)	1.78～1.86(m)
3-H	2.44(m)	2.16(m)	2.41(m)	2.35(m)
4-H	2.02(m)	2.01(m)	2.34(m)	1.96(brd,5)
5-H	2.24(dd,5,3)	2.22(dd,6,3)	2.63(t,2)	1.24(brs)
7-H	4.92(s)	4.69(s)	9.33(s)	4.97(d,11)
8-H	—	—	—	5.17(td,11,5)
9-H	5.42(五重峰,1)	5.42(五重峰,1)	6.02(五重峰,1)	1.72(dd,14,11) 1.93(dd,14,5)
11-H	2.99(brd,5)	2.68(brd,6)	3.51(brs)	2.28(brt,5)
12-CH_3	1.01(d,7)	1.03(d,7)	1.26(d,7)	0.94(d,7)
13-CH_3	1.25(s)	1.26(s)	1.09(s)	0.98(s)
14-CH_3	0.86(s)	0.85(s)	1.08(s)	0.92(s)
15-CH_3	1.80(d,1)	1.70(d,1)	2.06(d,1)	1.06(s)

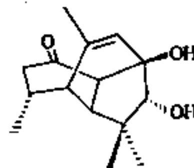




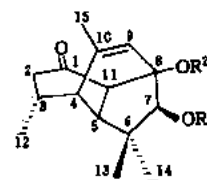
526. Ang = (—)



527

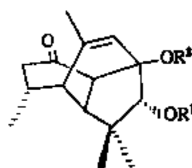


528



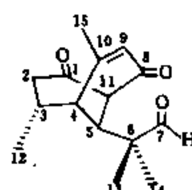
529. $R^1 = R^2 = Ac$

530. $R^1 = Ac$, $R^2 = H$

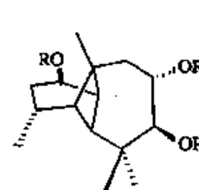


531. $R^1 = R^2 = Ac$

532. $R^1 = Ac$, $R^2 = H$



533



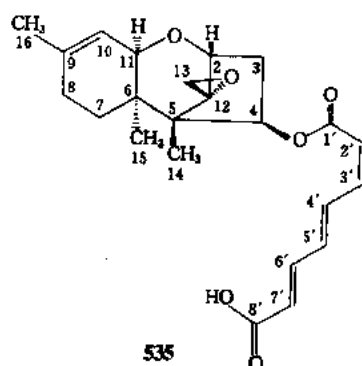
534. R = Ac

表 8-89 单端孢菌烷倍半萜化合物 535 的 ^{1}H-NMR 化学位移[132]

质子	δ	HMBC	NOESY	PS-COSY
2β-H	3.87d(5.2)	4,11,12	3α,3β,13α	3β
3α-H	2.59dd(15.4,7.8)	2,5,12	2β,3β,4α,11α	3β,4α
3β-H	2.05ddd(15.4,5.2,3.4)	4	2β,3α	3α,2β,4α
4α-H	5.66dd(7.8,3.4)	6,12,1′	3α,11α,15	3α,3β
5-H				
6-H				
7α-H	1.43m		7β,14,15	7β,8α,8β,11α
7β-H	1.94m		7α	7α,8α,8β
8α-H	2.00m			7α,7β,16
8β-H	2.00m			7α,7β,16
9-H				
10-H	5.42m	6,8,11,16	11α,16	11α,16
11α-H	3.65d(5.5)	9,10,15	3α,4α,10,15	10,7α
12-H				

续表

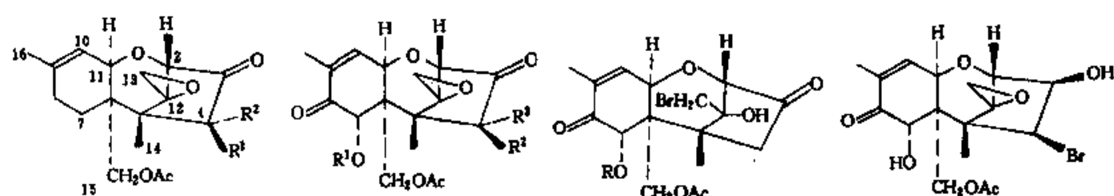
质　子	δ	HMBC	NOESY	PS-COSY
13α-H	3.16d(4.0)		2β,13β	13β
13β-H	2.86d(4.0)		13α,14	13α
14-H	0.73s	4,5,6	7α,13β	
15-H	0.97s	5,6,7	4α,7α	
16-H	1.72bs	8,9,10	10	8,10
1′-H				
2′-H	5.87d(11.3)	1′,4′	3′	3′
3′-H	6.66t(11.3)	1′,5′	2′,4′	2′,4′
4′-H	7.95ddd(15.3,11.3,0.6)	2′	3′	3′,5′
5′-H	6.57ddd(15.3,11.3,0.6)	3′	7′	4′,6′
6′-H	7.52ddd(15.3,11.3,0.6)	4′,8′	4′,5′	5′,7′
7′-H	6.03d(15.3)	8′	5′	6′
8′-H				



535

表 8-90　单端孢菌烷倍半萜化合物 536～547 的^{1}H-NMR 化学位移[133]

化合物 质子	536	537	538	539	540	541	542	543	544	545	546	547
2-H	3.52s	3.52s	3.65s	3.67s	3.55s	3.66s	3.78s	3.66s	3.55s	3.75s	3.77s	3.91s
4-H	5.97s	4.30s	4.30s	5.94s	5.61s	4.30d (6.5)	4.26s	6.04s	2.93d (α-) 2.35d	4.95s	2.60d 2.70d (19.0)	5.38d (5.9)
7-H	≈2.2	≈2.1	≈2.1	4.99d (1.7)	4.84d (2.0)	4.96d (1.8)	4.85s	6.06s	4.94d (19.4)	4.97d (1.8)	4.66d (1.6)	4.81d (1.5)
10-H	5.49d (5.8)	5.43d (5.7)	5.45d	6.55d (5.9)	6.62d (5.9)	6.50d (5.9)	6.59d (5.9)	6.53d	6.52d (5.9)	6.52d (5.9)	6.45d (5.3)	6.56d (5.9)
11-H	4.11d (5.8)	3.86d (6.0)	4.18d	4.61d	4.98d (5.9)	4.40d (5.9)	4.85d (5.9)	4.66d (5.8)	4.52d (5.9)	4.51d (5.9)	4.47d (5.3)	4.35d (5.9)
13-H	2.95d 3.16d (3.9)	2.95d 3.15d (3.5)	2.71d 3.02d (4.0)	3.20d 3.27d (4.2)	3.08s	3.18d 3.25d (4.1)	3.03s	2.76d 3.09d (3.6)	3.25d 3.36d (4.1)	3.15d 3.23d (4.2)	3.98d 4.50d (9.9)	3.05d 3.07d (9.1)
14-H	0.88s	0.99s	0.81s	1.16s	0.99s	1.28s	1.09s	1.00s	1.30s	1.46s	1.55s	1.34s
15-H	4.13d 4.21d (12.4)	4.04d 4.13d (12.4)	3.87d 4.19d (12.5)	4.02d 4.59d (12.6)	4.18d 4.54d (12.5)	4.21d 4.44d (12.4)	4.25d 4.34d (12.2)	4.18d 4.56d (12.6)	4.19d 4.31d (12.2)	4.11d 4.40d (12.5)	4.20d 4.41d (11.8)	4.05d 4.57d (12.3)
16-H	1.75s	1.73s	1.73s	1.93s	1.92s	1.92s	1.91s	1.91s	1.92s	1.93s	1.91s	1.91s
Ac	2.13 2.15	2.08	2.07	2.05 2.18	1.95 2.22	1.94	2.10	1.96 2.10 2.22	1.94	2.00	1.84	1.97
OH	—	2.63		3.84 (1.7)	3.82 (2.0)	2.34 3.89	3.87	—	3.83	3.95d (1.8)	2.80 3.91d (1.8)	2.50 3.87d (1.5)



	R^1	R^2
536.	OAc	H
537.	OH	H
538.	H	OH

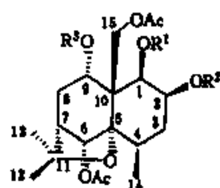
	R^1	R^2	R^3
539.	H	OAc	H
540.	H	H	OAc
541.	H	OH	H
542.	H	H	OH
543.	Ac	OAc	H
544.	H	H	H
545.	H	Br	H

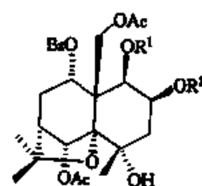
546. R=H

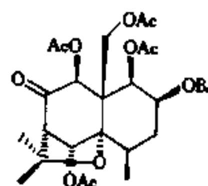
547

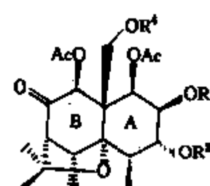
表 8-91　双氢琼脂呋喃型倍半萜化合物 548 ~ 554 的^{1}H-NMR 化学位移[134]

质子 \ 化合物	548	549	550	551	552	553	554
1-H	4.72dd (4.9,3.6)	5.71d(3.2)	5.70d(3.5)	5.71d(3.5)	5.67d(3.5)	5.71d(3.5)	5.98d(3.4)
2-H	5.33dd (3.6,7.3)	5.58dd (3.2,6.2)	5.53dd (3.5,6.8)	5.80dd (3.5,6.7)	5.56dd (3.5,6.7)	5.70dd (3.5,6.8)	5.49ddd(3.4, 2.5,1.1)
3-H	2.35ddd(14.0, 7.3,3.0)	2.53m	2.35ddd(14.3, 6.8,3.0)	2.28m	1.8~2.4m	2.41m	4.92dd (2.5,1.1)
	1.83dd (14.0,3.0)	1.80dd (15.0,2.4)	1.80dd (14.3,3.0)	2.19m	1.98dd (15.3,3.1)	2.00m	—
4-H	2.2~2.4m	2.39m	1.9~2.6m	—	—	2.49m	2.69brq (7.9)
4-OH-H	—	—	—	2.93s	2.89s	—	—
6-H	5.85s	5.97s	5.96s	6.17s	6.16s	6.42s	6.37d(0.9)
7-H	2.2~2.4m	2.0~2.6m	1.9~2.6m	2.23m	1.8~2.4m	3.07s	3.03d(0.9)
8-H	2.53ddd(15.5, 7.3,3.0)	2.56ddd(14.9, 7.2,2.5)	2.48ddd(16.0, 7.0,3.0)	2.62ddd(15.7, 7.2,3.4)	2.55m	—	—
	2.28dd (15.5,3.0)	2.22dd (14.9,2.5)	2.21dd (16.0,3.0)	2.27m	1.8~2.4m	—	—
9-H	5.48d(7.3)	5.41d(7.2)	5.43d(7.0)	5.51d(7.2)	5.35d(6.7)	5.62s	5.65s
12,13-H	1.50s,1.43s	1.45s,1.42s	1.42s,1.42s	1.59s,1.55s	1.55s^f,1.50s^f	1.45s,1.52s	1.45s,1.45s
14-H	1.16d(7.6)	1.19d(7.6)	1.19d(7.6)	1.56s	1.49s^f	1.29d(8.4)	1.29d(7.9)
15-H	4.87d(12.6) 4.45d(12.6)	5.05d(12.7) 4.36d(12.7)	5.04d(13.0) 4.36d(13.0)	5.29d(12.7) 4.48d(12.7)	5.03d(13.1) 4.41d(13.1)	4.90d(12.8) 4.81d(12.8)	4.83d(12.8) 4.69d(12.8)
2′,6′-Bz	8.07d(7.9)	8.04d(7.3)	—	8.11d(7.3), 8.05d(7.3)	8.03d(7.4)	8.05d(7.5)	—
4′-Bz	7.58t(7.4)	7.57t(7.4)	—	7.59t(7.1) (2H)	7.56t(7.5)	7.50t(7.6)	—
3′,5′-Bz	7.47t(7.8)	7.44t(7.6)	—	7.50t(7.8) 7.47t(7.6)	7.45t(7.7)	7.60m	—
Ac	2.22s 2.10s 2.10s	2.25s 2.11s 2.08s 1.55s	2.25s 2.11s 2.08s 1.59s	2.29s(C-15) 2.12s(C-6) 1.43s(C-1)	2.27s 2.11s	2.14s 2.09s 2.06s 1.93s	2.14s 2.14s 2.11s 2.06s 1.97s









	R^1	R^2	R^3
548.	H	Ac	Bz
549.	Ac	Ac	Bz
550.	Ac	Ac	Nic

	R^1	R^2
551.	Ac	Bz
552.	*i*Bu	*i*Bu

553

554

R^1-R^4 3 × Ac; 1 × Cin

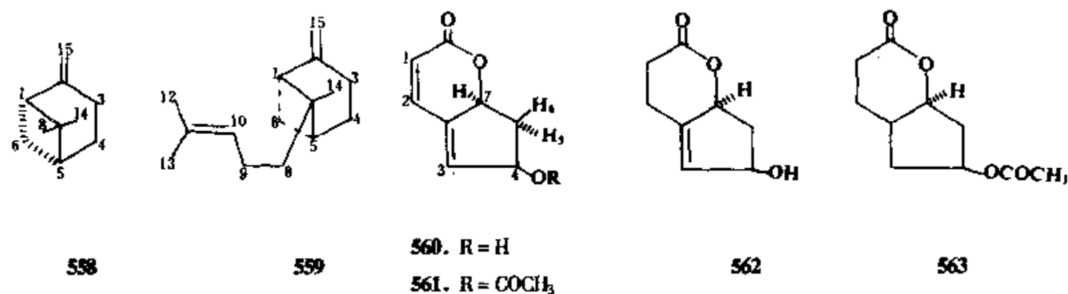
表 8-92 双氢琼脂呋喃型倍半萜化合物 555 ~ 557 的 ¹H-NMR 化学位移[135]

质子 \ 化合物	555	556	557
1-H	6.02(d,4.0)	5.80(d,4.30)	5.67(d,4.2)
2-H	5.55(dd,4.0,2.3)	5.43(dd,4.3,2.2)	5.48(dd,4.2,2.4)
3-H	4.87(d,2.3)	4.79(d,2.2)	4.78(d,2.4)
6-H	6.46(s)	7.02(s)	7.04(s)
7-H	2.43(d,3.2)	2.36(d,4.2)	2.38(d,4.2)
8-H	4.39(dd,3.2,9.5)	5.53(dd,4.2,5.9)	5.54(dd,4.2,6.1)
9-H	5.75(d,9.5)	5.38(d,5.9)	5.42(d,6.1)
13-H	3.72,5.97 (ABq,11.7)	3.69,5.95 (ABq,11.5)	3.72,5.98 (ABq,11.6)
15-H	4.44,5.46 (ABq,13.1)	4.19,5.58 (ABq,13.4)	4.16,5.54 (ABq,13.5)
4″-H	8.08(dd,1.6,7.5)	8.06(dd,1.8,8.0)	8.06(dd,1.8,7.8)
5″-H	7.26(dd,3.9,7.5)	7.26(dd,4.9,8.0)	7.32(dd,4.8,7.8)
6″-H	8.69(dd,1.6,3.9)	8.68,(dd,1.8,4.9)	8.70(dd,1.8,4.8)
3‴-H	6.57(d,9.6)	6.57(d,9.6)	6.59(d,9.6)
4‴-H	7.82(dd,2.5,9.6)	7.87(dd,2.6,9,6)	7.90(dd,2.5,9.6)
6‴-H	8.36(d,2.5)	8.43(d,2.6)	8.42(d,2.5)
2′-H	2.63(q,6.9)	2.56(q,7.1)	2.57(q,6.8)
3′-H	4.66(q,7.0)	4.66(q,7.0)	4.67(q,7.0)
4′-Me	1.24(d,7.1)	1.19(d,7.0)	1.20(d,7.0)
5′-Me	1.40(d,7.1)	1.37(d,7.0)	1.39(d,7.0)
12-Me	1.82(s)	1.71(s)	1.71(s)
14-Me	1.58(s)	1.52(s)	1.57(s)
OAc	1.45(C-9)	1.80(C-9)	1.81
OAc	2.20(C-15)	2.11	1.98
OAc	2.30(C-6)	2.19	2.18
OAc	—	2.36(C-6)	2.22
OAc	—	—	2.38
2⁗,6⁗-H	7.70(d,7.5)	—	—
3⁗,5⁗-H	7.33(t,7.5)	—	—
4⁗-H	7.49(t,7.5)	—	—
4'''''-Me	—	1.65(d,8.5)	—
5'''''-Me	—	1.63(s)	—
3'''''-H	—	6.52(q,8.5)	—

	R^1	R^2	R^3
555.	C_6H_5COO	H	OH
556.	$CH_3CH_2CH(CH_3)COO$	OAc	H
557.	OAc	OAc	H

表 8-93 其他倍半萜类化合物 558～563 的 ^1H-NMR 化学位移[66,122]

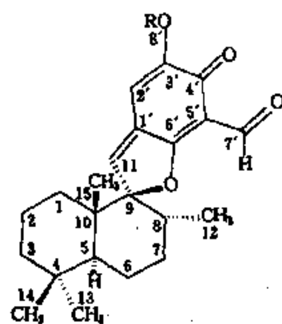
质子 \ 化合物	558	559	560	561	562	563
1-H	2.46t	2.53t	6.37dd(10,1.5)	6.16dd(10,1.5)	2.75m(e) 2.30m(a)	2.40m
2-H	—	—	6.65dd(10,2)	6.68dd(10,2)	2.30m(e) 1.40m(a)	1.67(m)
3-H_α	2.55ddd	2.56bddd	5.87s	5.87s	5.75s	2.00m
3-H_β	2.25ddd	2.25bddd				
4-H	1.84m	1.84m	4.67m(13,5)	5.67m	3.87m(8,3)	4.52m
5-H	1.97dd	2.07dd	2.94m	2.94m	2.30m	1.67m
6-H_α	1.42d	1.43d	1.68m	1.75m	1.70m	1.67m
6-H_β	2.31dt	2.30dt	—	—	—	—
7-H	—	—	4.93ddd	4.96ddd	4.71ddd	—
8-H	1.24s	1.61m	~2.0	—	~2.31m	—
9-H	—	1.95bq	—	—	—	—
10-H	—	5.16bt	—	—	—	—
12-H	—	1.71bs	—	—	—	—
13-H	—	1.61bs	—	—	—	—
14-H	0.72s	0.72s	—	—	—	—
15-H_α	4.63m	4.63m	—	—	—	—
15-H_β	4.16m	4.56m	—	—	—	—



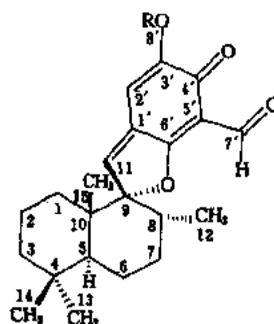
558　559　560. R = H　561. R = COCH$_3$　562　563

表 8-94　其他倍半萜类化合物 564～567 的^{1}H-NMR 化学位移[136]

质子＼化合物	564	565	566	567
7′-H	10.27s	10.31s	10.28s	10.31s
11-H	7.50s	7.25s	7.38s	7.13s
2′-H	6.48s	6.43s	6.27s	6.22s
8′-H	7.40brs(OH)	7.40brs(OH)	3.84s(OCH_3)	3.82s(OCH_3)
8-H	2.61m	2.42m	2.61m	2.42m
1,2,3,6,7-H	2.00～0.80m	1.80～0.80m	2.00～0.80m	2.00～0.80m
5-H	1.24dd(2.9,12.0)	1.75dd(2.7,12.2)	1.24dd(2.9,12.5)	1.79dd(2.6,13.2)
15-CH_3	1.36s	1.28s	1.36s	1.26s
13-CH_3	0.94s	0.95s	0.94s	0.95s
14-CH_3	0.91s	0.88s	0.91s	0.87s
12-CH_3	0.55d(6.6)	0.56d(6.6)	0.56d(6.6)	0.56d(6.6)



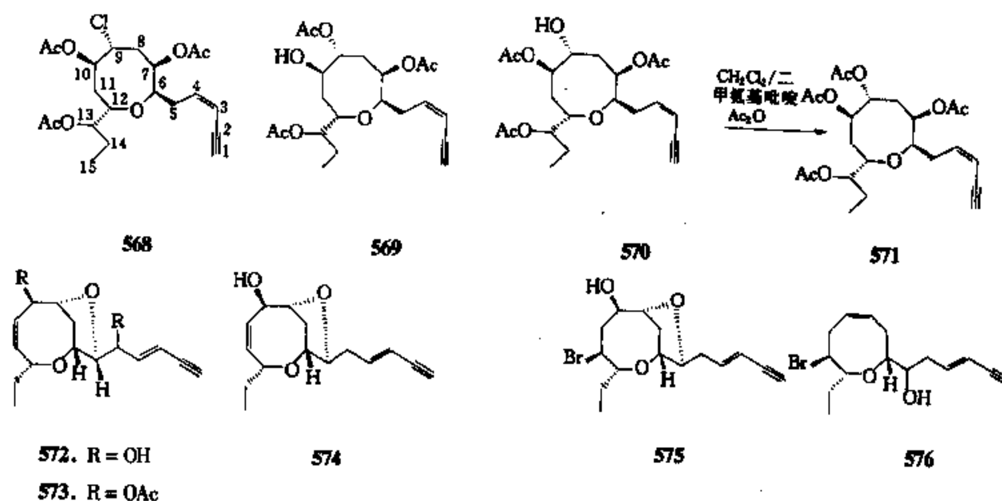
564. R = H
566. R = CH_3



565. R = H
567. R = CH_3

表 6-95 其他倍半萜类化合物 568～576 的 ¹H-NMR 化学位移[137]

质子＼化合物	568	569	570	571	572	573	574	575	576
1-H	3.11d(2.2)	3.14dd(0.8,2.2)	3.10dd(0.8,2.3)	3.12dd(0.7,2.3)	2.90d(2.2)	2.90d(2.4)	2.64d(2.2)	2.62d(2.3)	2.61dd(0.6,2.2)
2-H	5.43brd(10.9)	5.45brd(10.8)	5.43dddd(1.0,1.0,2.3,10.4)	5.44brd(10.8)	5.88ddd(2.1,2.2,16.1)	5.77ddd(1.3,2.4,16)	5.60dddd(1.7,2.2,3.8,15.8)	5.57dddd(1.5,2.1,3.8,15.8)	5.68dddd(1.6,1.6,2.3,16.0)
4-H	5.73ddd(7.7,7.7,10.9)	5.75dddd(0.8,7.4,7.4,10.8)	5.81dddd(1.0,7.6,7.6,10.4)	5.72br ddd(7.5,7.5,10.8)	6.39dd(4.8,16.1)	6.30ddd(0.7,6.4,16.1)	6.33ddd(7.4,7.5,15.8)	6.26ddd(7.3,7.4,15.8)	6.36dddd(0.6,7.2,7.4,16.0)
5-H	2.61brdd(7.4,7.7)	2.67m,2.82m	2.67ddd(1.0,7.4,7.6),2.76ddd,J=(1.0,7.4,7.6)	2.67m,2.80ddd(7.5,9.4,13.8)	4.46ddd(2.1,4.8,6.7)	4.57m	2.54m	2.36m	1.97m
6-H	3.61brdd(7.2,7.4)	3.73m	3.69brdd,J=(7.4,7.6)	3.65dd(5.2,9.4)	3.73dd(2.8,6.7)	3.84dd(2.6,9.1)	3.52ddd(2.6,7.1,7.4)	3.38ddd(2.4,7.1,7.3)	3.22ddd(4.2,5.3,7.8)
7-H	4.76brd(5.1)	4.79brd(4.8)	4.80brd(4.7)	4.78brd(5.0)	4.32ddd(1.4,2.5,2.8)	4.16ddd(1.4,2.5,2.6)	3.37m	3.27ddd(1.1,2.3,2.4)	2.78ddd(1.4,5.3,10.5)
8-H	1.58m,2.55dd(5.1,16.6)	1.84ddd(2.4,9.1,15.7),2.20dd(4.8,15.7)	1.86ddd(2.3,8.8,16.1),2.15dd(4.7,16.1)	1.87ddd(2.0,9.5,16.0),2.21dd(5.0,16.0)	1.77ddd(2.5,7.1,13.7),2.70dd(1.4,13.7)	1.81ddd(2.5,7.2,13.7),2.73dd(1.4,13.7)	1.27ddd(2.4,7.1,13.3),2.32dd(1.3,13.3)	1.16ddd(2.3,8.0,14.2),1.88br d(14.2)	1.67ddd(1.4,8.5,14.2),2.12m
9-H	5.21dd(8.8,9.9)	5.74brdd(8.9,9.1)	4.78dd(8.8,8.8)	6.02dd(9.3,9.5)	4.25dd(3.5,7.1)	4.35dd(3.9,7.2)	4.25dd(3.4,7.1)	4.04dd(3.6,8.0)	5.67dddd(1.0,6.9,8.2,10.6)
10-H	5.28ddd(2.3,4.1,9.9)	3.72m	4.94ddd(2.7,4.3,8.8)	5.27ddd(2.3,4.3,9.3)	5.02ddd(2.4,7.4,9.5)	5.88m	5.04ddd(2.1,2.2,3.4)	3.72ddd(1.5,3.6,9.8)	5.79dddd(2.0,6.3,9.4,10.6)
11-H	1.71m,1.98ddd(1.9,4.1,16.6)	1.78m,1.82ddd(2.5,3.8,15.7)	1.73m,1.96ddd(2.1,4.3,16.5)	1.73m,1.92m	5.44ddd(2.4,3.5,12.1)	5.15dddd(0.6,2.2,4.3,12.1)	5.17ddd(2.2,2.3,11.9)	2.04m,2.26ddd(1.3,4.7,14.7)	2.29ddd(3.3,6.3,14.0),2.85dddd(1.0,3.7,9.4,14.0)
12-H	4.07ddd(1.9,8.4,12.2)	4.33dddd(0.5,2.5,8.6,11.4)	4.09ddd(2.1,8.5,12.5)	4.40br ddd(2.0,8.3,12.4)	5.59ddd(2.4,4.0,12.1)	5.56m	5.55ddd(2.1,4.3,11)	3.50ddd(4.7,10.4,10.6)	3.80ddd(3.3,3.7,10.0)
13-H	5.40ddd(3.8,8.3,8.4)	5.10ddd(3.6,8.3,8.6)	5.06ddd(3.8,8.3,8.3)	5.07ddd(3.5,8.2,8.1)	3.87m	3.81m	3.50m	3.09brdd(2.7,9.9,10.6)	3.35ddd(2.7,6.9,10.0)
14-H	1.54m,1.84m	1.63m,1.96m	1.58m,1.89m	1.58m,1.92m	1.52m,1.60m	1.52m	1.33m	1.52m,2.01m	1.46m,1.84m
15-H	0.83dd(7.5,7.5)	0.90dd(7.5,7.5)	0.86dd(7.5,7.5)	0.87dd(7.5,7.5)	0.95dd(7.5,7.5)	0.96dd(7.5,7.5)	0.85dd(7.3,7.5)	0.81dd(7.4,7.4)	0.82dd(7.4,7.4)
OAc	1.69s,1.77s,1.96s	1.57s,1.71s,2.19s	1.65s,1.72s,1.81s			2.18s,2.09s			



568　569　570　571

572. R = OH
573. R = OAc
574　575　576

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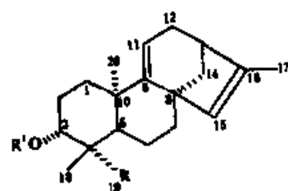
第九章 二萜及三萜类化合物的^{1}H-NMR化学位移和偶合常数

第一节 二萜类化合物的^{1}H-NMR化学位移

一、贝壳松烷衍生物的^{1}H-NMR化学位移

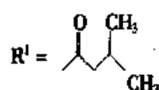
表 9-1 贝壳松烷衍生物 1～6 的^{1}H-NMR化学位移[1]

质子 \ 化合物	1	2	3	4	5	6	质子 \ 化合物	1	2	3	4	5	6
3-H	4.60dd	4.64dd	3.43dd	3.41dd	4.58d	4.56dd	19-H_A	—	—	4.27d	4.17d	—	—
11-H	4.95bdd	4.96bdd	4.92bdd	4.95bdd	—	—	19-H_B	—	—	3.62bd	3.48d	—	—
12-H_A	2.21ddd	2.21ddd	2.19ddd	2.19ddd	—	—	20-H	1.08s	1.10s	0.99s	1.10s	1.02s	1.02s
12-H_B	1.9m	1.9m	1.9m	1.9m	—	—	OCH_3	3.70s	3.71s	—	—	3.68s	3.65s
13-H	2.45bdd	2.46bdd	2.45bdd	2.46bdd	2.35bs	2.38bs	OCOR	2.36d	6.77qq	—	—	2.20bd	2.35m
15-H	5.69bs	5.69bs	5.70bs	5.70bs	5.30bs	5.40bs		1.13d	1.79bs	—	—	0.96d	1.14d
17-H	1.71d	1.72d	1.72d	1.72d	1.74d	1.74d		1.11d	0.77bd	—	—	—	—
18-H	1.25s	1.25s	1.22s	1.31s	1.24s	1.24s							



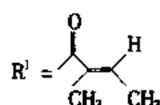
1. R = CO_2CH_3,

R^1 =



2. R = CO_2CH_3

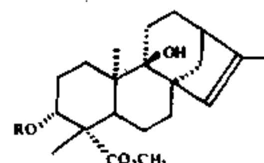
R^1 =



3. R = CH_2OH,

R^1 = H

4. R = —CH_2—O—C(CH_3)$_2$—R^1



5. R =

6. R =

表 9-2 贝壳松烷衍生物 7～12 的^{1}H-NMR化学位移[2]

质子 \ 化合物	7	8	9	10	11	12
3-H_α	2.18bd	2.18bd	2.33bd	2.32bd	2.33bd	—
3-H_β	0.79ddd	0.80ddd	0.80ddd	0.81ddd	0.81ddd	4.52dd
12-H	3.79bdd	4.76bdd	—	—	—	—
13-H	2.64bdd	2.76bdd	2.64bdd	2.66bdd	2.65bdd	2.64bdd
17-H_A	4.86bs	4.96bs	4.80bs	4.85bs	4.80bs	4.80bs
17-H_B	4.78bs	4.84bs	4.74bs	4.79bs	4.74bs	4.74bs
18-H	1.17s	1.26s	3.98d	3.92d	3.93d	1.22s
					3.47d	
20-H	0.99s	1.02s	0.87s	0.88s	0.88s	0.91s
OCH_3	3.64s	—	3.67s	3.65s	3.70s	3.67s
OCOR	—	—	5.66qq	2.18bd	—	2.22bd
	—	—	2.14d	0.94d	—	—
	—	—	1.88d	—	—	—

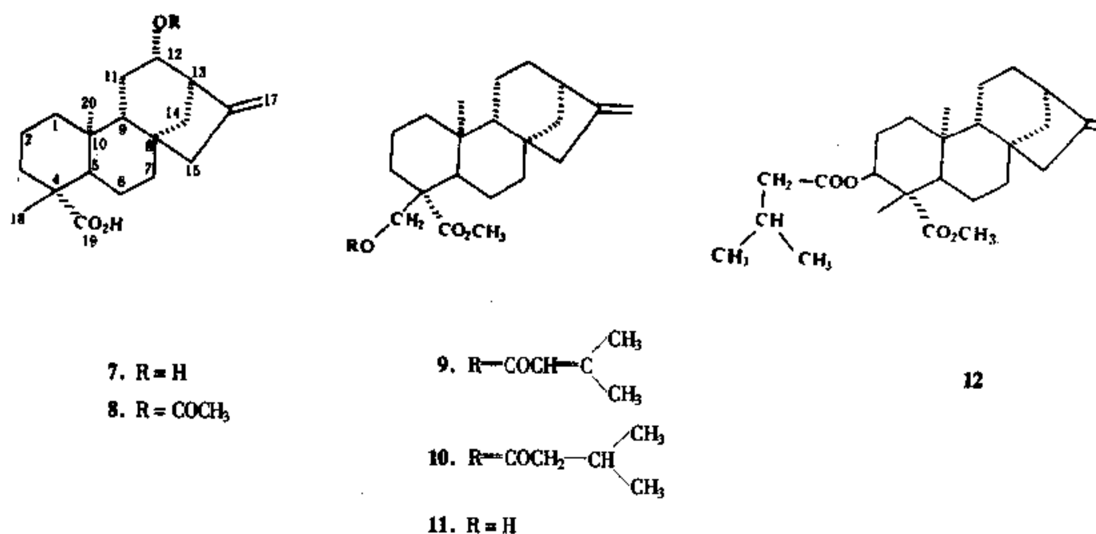


表 9-3 贝壳松烷衍生物 13～21 的^{1}H-NMR 化学位移[2,3,4]

质子＼化合物	13	14	15	16	17	18	19	20	21
3-H$_α$	—	—	—	2.17bd	2.18bd	2.17bd	3.57bd		
3-H$_β$	—	4.58dd	4.74dd	0.78ddd	0.80ddd	0.80ddd	1.62ddd		
11-H$_A$	—	—	—	—	—	2.55dd	5.14dd		
11-H$_B$	—	—	—	—	—	2.20bd	4.94bd		
12-H	—	—	—	4.75bdd	3.79bdd	—	—		
13-H	—	—	—	2.76bdd	2.64bdd	3.22bd	5.68bs	2.65m	3.05m
17-H$_A$	2.88d	2.89d	2.89d	4.95bs	4.85bs	4.99bs	5.63bs	4.79bs	}9.74s
17-H$_B$	2.80s	2.81d	2.81d	4.83bs	4.78bs	4.87bs	5.38bs	4.73bs	
18-H	4.35d	1.08s	0.95s	1.19s	1.18s	1.19s	2.35s	1.04s	1.18s
	3.93d								
19-H$_A$	0.98s	—	10.12s	—	—	—	—	4.23d	—
19-H$_B$	—	—	—	—	—	—	—	3.89dd	—
20-H	1.08s	0.90s	1.12s	0.90s	1.01s	0.70s	2.15s	0.95s	0.88s
OCH$_3$	—	—	—	3.67s	3.64s	3.64s	4.60s	—	3.66s

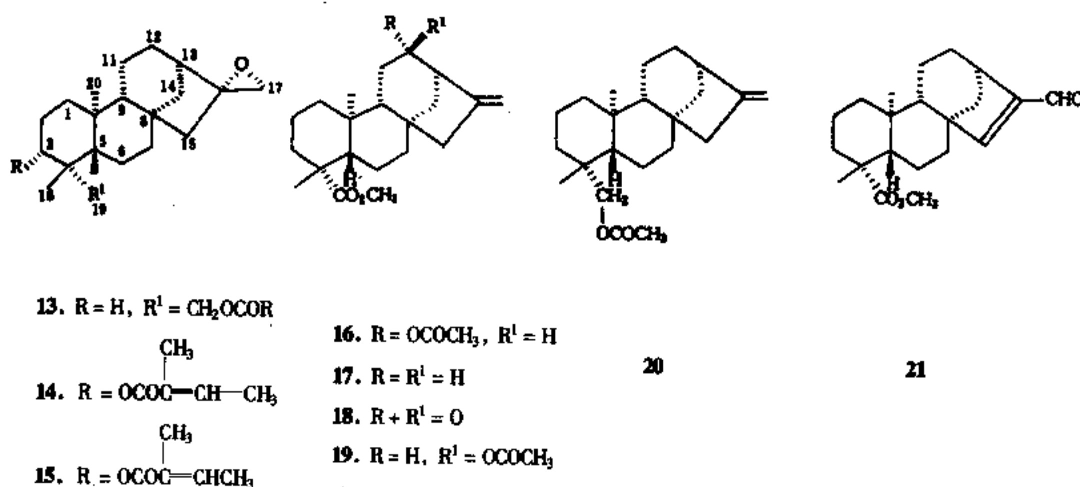
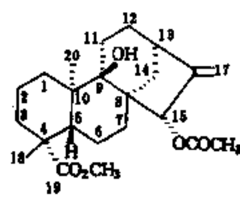
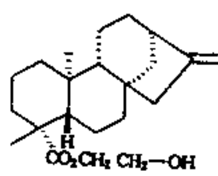


表 9-4 贝壳松烷衍生物 22 ~ 30 的 ^{1}H-NMR 化学位移[5]

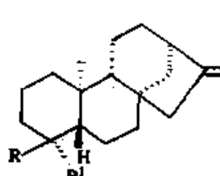
质子 \ 化合物	22	23	24	25	26	27	28	29	30
3-Hα	—	—	—	—	1.05ddd	—	1.00ddd	—	3.41dd
3-Hβ	—	2.19bd	—	—	2.21bd	2.16bd	2.17bd	2.18bd	—
13-H	2.78m	2.64m	2.65m	2.65m	3.39d	2.77m	2.55m	—	—
15-H	5.98bs	2.05m	2.07m	2.08m	2.53bd	4.12bs	5.36bs	4.70bs	4.97dd
					2.38ddd				4.91dd
17-H	5.12bs	4.80bs	4.80bs	4.80bs	5.25bs	5.21bs	4.20bs	3.04d	1.13s
		4.74bs	4.74bs	4.71bs	4.99bs			2.76d	
18-H	1.17s	1.20s	1.17s	0.98s	1.23s	1.20s	1.17s	1.18s	0.95s
19-H	—	—	—	—	—	—	—	—	0.82s
20-H	0.98s	0.87s	1.17s	1.13s	1.07s	0.97s	0.86s	0.86s	0.74s
OCH_3	3.65s	—	—	—	3.61s	3.66s	3.64s	3.65s	—

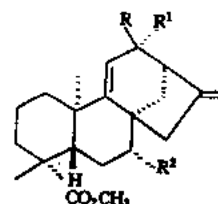


22



23



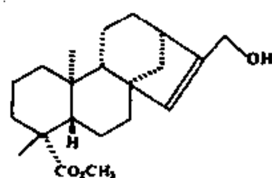


24. R = CH_3, R¹ = OH

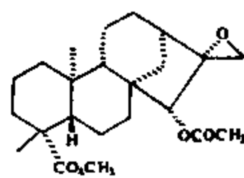
25. R = OH, R¹ = CH_3

26. R + R¹ = O, R² = H

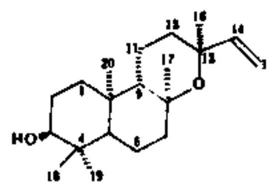
27. R = R¹ = H, R² = OH



28



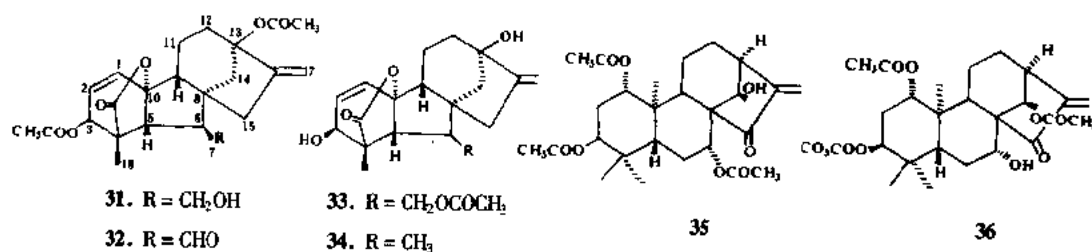
29



30

表 9-5 贝壳松烷衍生物 31 ~ 36 的 ^{1}H-NMR 化学位移[5]

质子 \ 化合物	31	32	33	34	35	36
1-H	6.37d(9)	6.36d(9)	6.33d(9)	6.29d(9)	4.8 ~ 4.92dd	4.64 ~ 4.90dd
2-H	5.80dd(9,4)	5.88dd(9,4)	5.87dd(9,4)	5.80dd(9,4)	—	—
3-H	5.29d(4)	5.33d(4)	4.15d(4)	4.12d(4)	4.72t(3)	4.64 ~ 4.90dd
5-H	2.65d(10)	3.33d(10)	2.56d(10)	2.31d(10)	—	—
6-H	—	2.86dd(10,2)	—	1.92m	—	—
7-H	3.82dd	9.83d(2)	4.25dd	1.04d(7)	5.40dd	4.12d
	3.73dd		4.05dd			
13-H	—	—	—	—	3.10m	3.08m
14-H	—	—	—	—	4.86bs	5.98bs
15-H	2.87dt(16,3)	2.60dt(15,3)	2.63dt(16,3)	2.48dt(15,3)	—	—
17-H	5.10d	5.17d	5.27d	5.23d	5.40bs	5.36bs
	4.97d	5.02d	5.10d	4.97d	6.14bs	6.12bs
18-H	1.25s	1.11s	1.37s	1.36s	1.30s	1.36s
19-H	—	—	—	—	0.90s	0.88s
20-H	—	—	—	—	0.94s	0.96s

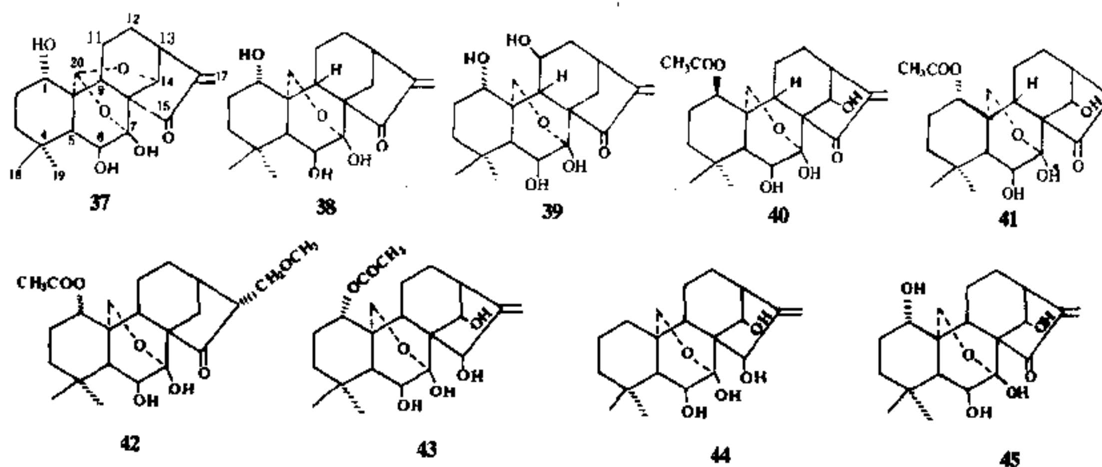


31. R = CH_2OH　　33. R = CH_2OCOCH_3　　35　　36

32. R = CHO　　34. R = CH_3

表 9-6　贝壳松烷衍生物 37～45 的 ^{1}H-NMR 化学位移[6~8]

质子 \ 化合物	37	38	39	40	41	42	43	44	45
1-H	3.82t(8)	3.62dd(8)	4.19t (6.5)	4.74dd (10,6)	4.62t	4.5～5.0m	4.88dd (8,10)	—	3.68t(8)
5-H	1.66bs	—	—	—	—	—	1.65d(6)	1.32d(5)	—
6-H	4.24bs	4.19dd (11,7)	4.25d(6)	4.12d (6.5)	3.81	3.93bd	4.22m	3.82d(5)	4.30bs
9-H	—	—	—	—	—	—	2.7～3.1m	2.37dd(9,2)	—
11-H	—	—	4.16m	—	—	—	—	3.91m	—
13-H	3.10m 3.24m	—	—	3.14d(10)	—	—	2.7～3.1m	2.71d(9)	3.17d(9)
14-H	5.06d(6)	—	—	5.13d(2)	4.86	4.5～5.0m	5.05s	4.50s	5.34s
15-H	—	—	—	—	—	—	5.33bs	5.34bs	—
17-H$_A$	5.31bs	5.23bs	5.42bs	5.43bs	5.55bs	3.5～3.9	5.65bs	5.16bs	5.53bs
17-H$_B$	6.21bs	5.92bs	5.93bs	6.18bs	6.18bs			5.21bs	6.30bs
18-H	0.95s	1.12s	1.06s	1.07s	1.14s	1.15s	1.13s	1.03s	1.13s
19-H	1.09s	1.17s	1.16s	1.24s	1.14s	1.15s	1.14s	1.09s	1.28s
20-H$_A$	5.94s	4.29d	4.40d(10)	4.22d(10)	4.22s	4.21s	4.35d(10)	3.87d(10)	4.42d(10)
20-H$_B$		4.70d	4.61d(10)	4.47d(10)			4.57d(10)	4.14d(10)	4.75d(10)
OCH_3	—	—	—	—	—	3.40s	—	—	—

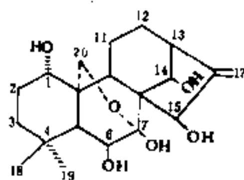


37　38　39　40　41

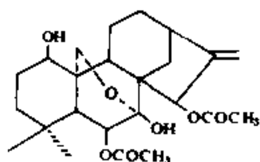
42　43　44　45

表 9-7　贝壳松烷衍生物 46～55 的^{1}H-NMR 化学位移[9～11]

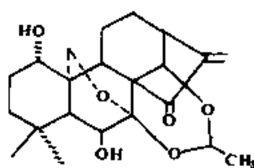
质子 \ 化合物	46	47	48	49	50	51	52	53	54	55
1-H	3.72t (7)	3.55bs	3.56t(8)	3.58t (2)		4.64～4.90m	4.80～4.92m	3.48 (10,6)	—	—
2-H	—	—	—	—	3.97tt (12,4)	—	—	—	4.42ddd	4.10m
3-H	—	—	—	—	—	4.64～4.90m	4.72t(3)	—	5.36d	—
5-H	—	—	—	1.93d (7)	—	—	—	—	—	—
6-H	4.23d (5)	5.18d	4.18d(7)	5.21d	—	—	—	—	—	—
7-H	—	—	—	—	4.45dd (13,5)	4.12dd (10,6)	5.40dd (12,4)	4.87dd (11,8)	4.84dd	4.08dd (10,6)
11-H	—	—	—	—	—	—	—	3.98	—	—
13-H	—	—	3.06d(7)	—	—	3.08m	3.10m	3.67d(4)	3.24m	3.08m
14-H	5.08s	—	4.66s	—	4.90bs	5.98bs	4.86bs	5.99s	5.12bs	4.96d(1)
15-H	5.32s	5.62s	—	5.62bs	—	—	—	—	—	—
17-H$_A$	5.62bs	4.90bs	5.42bs	4.91d (1)	5.25bs	5.36bs	5.40bs	5.38bs	5.36bs	5.29bs
17-H$_B$		5.03bs	6.14bs	5.04d (1)	6.13bs	6.12bs	6.14bs	6.31bs	6.29bs	5.87bs
18-H	1.20s	0.87s	1.16s	0.87s	0.85s	0.88s	0.90s	0.83s	0.94s	0.89s
19-H	1.23s	1.13s	1.29s	1.13s	0.90s	0.96s	0.94s	0.86s	0.98s	1.06s
20-H$_A$	4.38d (10)	3.91s	4.29d (10)	3.92s	1.04s	1.36s	1.30s	1.19s	1.16s	1.46s
20H$_B$	4.80d (10)		4.66d (10)							
O–CH(O)–H	—	—	5.62q	—	—	—	—	—	—	—
O–C(CH$_3$)–O	—	—	1.29d(5)	—	—	—	—	—	—	—



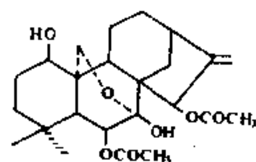
46



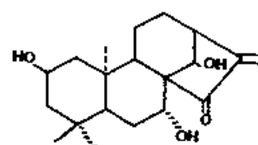
47



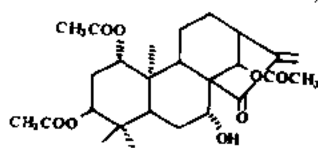
48



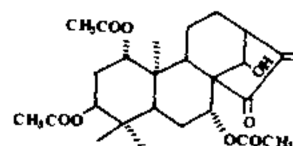
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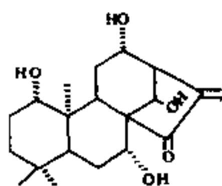
50



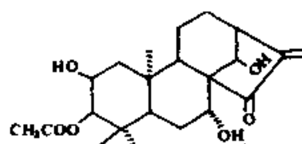
51



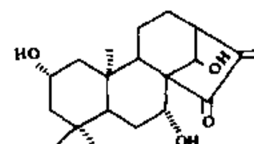
52



53



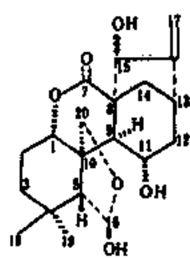
54



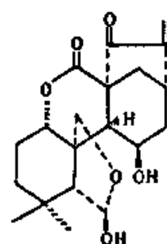
55

表 9-8 贝壳松烷衍生物 56~65 的 ^{1}H-NMR 化学位移[12~15]

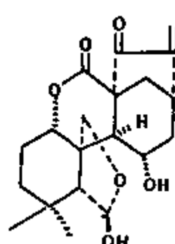
化合物 质子	56	57	58	59	60	61	62	63	64	65
1-H	4.87t(8)	4.84t(4)	4.92t(9)	5.25t(7)	5.12t(8)	5.12m	4.44t(9)	5.75dd (7,10)	4.67dd (7,7)	4.42dd (8,10)
3-H	—	—	—	3.85bs	—	—	—	—	—	—
5-H	3.17bs	2.47bs	3.25bs	2.82bs	2.72m	3.5s	1.96s	2.97d(5)	2.48d(5)	2.86s
6-H	5.71bs	5.50bs	5.71bs	—	4.25m	—	5.44s	6.27d(5)	6.00d(5)	4.72s
9-H	3.57d(10)	—	—	—	2.68d(11)	—	2.72dd (12,5)	—	—	2.12d(10)
11-H	4.40m	5.59t(8)	4.3~4.8m	—	4.00m	3.95m	3.00m	—	—	4.10m
13-H	—	3.13q(4)	—	—	3.10dd (10,4)	—	—	—	—	3.08dd (4,10)
14-H	—	3.51d(11)	—	—	—	—	2.42d(12)	—	—	2.40d(12)
15-H	5.54bs	—	—	—	—	—	—	—	—	—
17-H$_A$	5.25bs	5.30bs	5.98bs	1.00d	5.60bs	5.57bs	5.34d(1)	5.54bs	5.32m	5.91bs
17-H$_B$		5.90bs	5.33bs		6.10bs	6.03bs	5.93d(1)	6.22bs		6.00bs
18-H	1.00s	0.98s	0.98s	1.10s	1.04s	0.99s	1.01s	—	1.14s	1.00s
19-H	1.00s	0.98s	0.98s	1.48s	1.04s	0.99s	1.01s	3.56d(9) 4.18d(9)	4.05d(9) 3.57d(9)	1.00s
20-H$_A$	4.53d(9)	4.11t (10)	4.42d(10)	4.30d(10)	4.88d(12)	5.12d(12)	4.04t (10)	4.27d(10)	3.85d(10)	3.82d(10)
20-H$_B$	4.19d(9)		4.28d(10)	4.61d(10)	4.30d(12)	4.84d(12)		4.22d(10)	4.10d(10)	4.02d(10)



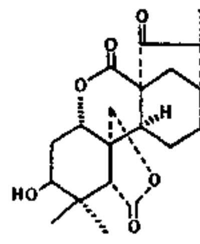
56



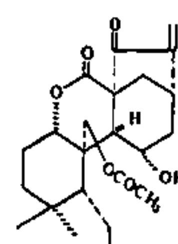
57



58



59



60

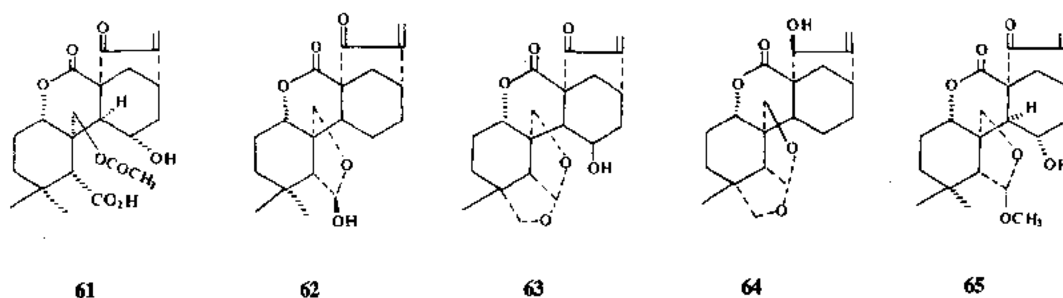
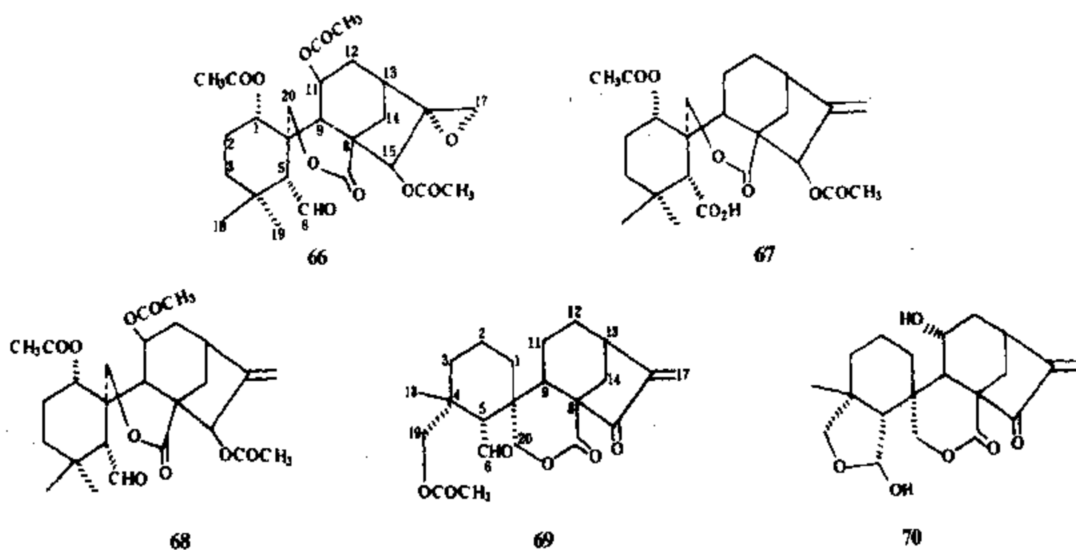


表 9-9 贝壳松烷衍生物 66～70 的 ^{1}H-NMR 化学位移[16,17]

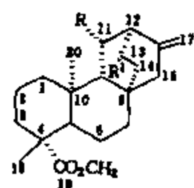
质子 \ 化合物	66	67	68	69	70
1-H	4.74dd(11,5)	5.13dd(8,8)	4.73dd	—	—
2-H	1.95m	1.90m	1.91m	—	—
3-H	1.53mm	1.59m	1.55m	—	—
5-H	3.15d(3)	3.67s	3.19d	1.92d(3)	1.93d(5)
6-H	9.94d(2,8)	—	9.99d(3)	4.85d	9.75d(5)
9-H	3.05d(10)	2.49d(11)	2.99d(11)	—	—
11-H	5.01ddd(10,10,8)	3.99ddd	4.95ddd	3.08dd	—
12-H_A	2.58dd	2.63ddd	2.82ddd	—	—
12-H_B	1.34dd	1.34dd	1.27ddd	—	—
13-H	2.58m	2.77dddd	1.75m	2.35m	2.15m
14-H_A	1.73d(13)	1.61d(13)	1.60d(12)	—	2.52dd
14-H_B	2.58m	2.17dd	2.28ddd	—	—
15-H	5.28s	5.59dd(3,2)	5.60dd	—	—
17-H_A	2.79d(4)	5.00d	5.01d	5.45bs	5.75bs
17-H_B	2.93d(4)	5.21d	5.18d	6.00bs	6.25bs
18-H	1.06s	1.00s	1.09s	1.15s	1.02s
19-H	1.15s	1.22s	1.12s	3.50d(9)	3.55d(15)
				3.70d(9)	3.75d(15)
20-H_A	4.70d(12)	4.62d(13)	4.82d(13)	4.06d(12)	4.16d(18)
20-H_B	4.86d(12)	5.00d(13)	5.01d(13)	4.24d(12)	4.22d(18)



二、阿替烷衍生物的^{1}H-NMR化学位移

表 9-10　阿替烷衍生物 71～77 的^{1}H-NMR 化学位移[18]

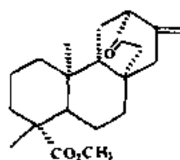
质子 \ 化合物	71	72	73	74	75	76	77
2-H_α	—	—	—	1.93dddd	—	—	—
3-H_α	2.16bd	2.17bd	2.17bd	2.18m	—	2.17bd	2.18bd
3-H_β	—	0.87ddd	0.89ddd	0.88ddd	—	—	—
11-H_A	5.27ddd	—	1.96bd	1.1m	1.96bd	—	—
11-H_B	—	—	—	1.7m		—	—
12-H	2.29ddd	2.45bddd	2.26bddd	2.93dd	2.28bddd	2.41bddd	2.41bddd
13-H	—	4.92dddd	4.01bd	—	4.01bd	4.87dddd	4.85bd
14-H_α	—	—	1.90ddd	2.67dd	1.85ddd	—	—
14-H_β	—	—	1.80bd	1.78d	1.20bd	—	—
15-H	—	—	—	2.22bd 2.13bd	—	—	—
17-H_A	4.87ddd	4.89ddd	4.85ddd	4.94ddd	4.84ddd	4.89ddd	4.89bs
17-H_B	4.70ddd	4.72ddd	4.69ddd	4.84ddd	4.68ddd	4.73ddd	4.73ddd
18-H	1.17s	1.17s	1.18s	1.19s	1.05s	1.18s	1.18s
19-H	—	—	—	—	3.76bd 3.46bd	—	—
20-H	1.08s	0.81s	0.88s	0.65s	0.96s	0.82s	0.83s
OCH_3	3.65s	3.63s	3.64s	3.63s	—	3.65s	3.64s



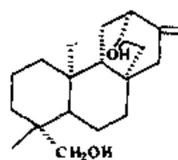
71. R = $OCOCH_3$, R^1 = H

72. R = H, R^1 = $-COC(CH_3)=CHCH_3$

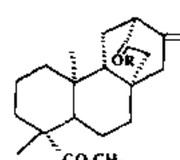
73. R = H, R^1 = OH



74



75



76. R = $COCH_2CH(CH_3)_2$

77. R = $COCH(CH_3)_2$

三、海松烷衍生物的¹H-NMR 化学位移

表 9-11　海松烷衍生物 78～84 的¹H-NMR 化学位移[19]

质子 \ 化合物	78	79	80	81	82	83	84
1-H	—	1.79dddd 1.61m	—	—	—	—	
2-H_α	2.54ddd	2.54ddd	—	—	—	—	—
2-H_β	2.40ddd	2.40ddd	—	—	—	—	—
3-H	—	—	3.49bs	3.49bs	—	3.46dd	3.74bs
6-H	5.64ddd	5.64ddd	5.58ddd	5.58ddd	—	—	5.66ddd
7-H_α	—	1.84bd	—	1.71m	}5.34bd	5.37ddd	1.70m
7-H_β	—	1.72m	—	1.71m			
10-H	—	2.23m	—	1.98m	—	—	—
15-H	3.78bd	3.92m	3.77m	3.91m	—	3.74dd	3.91m
16-H_A	3.37d	}3.78m	3.55m	3.76m	3.3～3.9m	3.68dd	}3.76m
16-H_B	3.57dd					3.56dd	
17-H	0.96s	0.94s	0.93s	0.91s	0.93s	0.95s	0.92s
18-H	1.26s	1.26s	1.15s	1.14s	0.98s	0.97s	0.88s
19-H	1.24s	1.24s	1.06s	1.06s	0.82s	0.88s	3.99d 3.49d
20-H	0.70s	0.71s	0.72s	0.71s	0.67s	0.82s	0.75s
—O, —O $C(CH_3)_2$	—	—	—	1.35s 1.41s	—	—	1.43s 1.45s

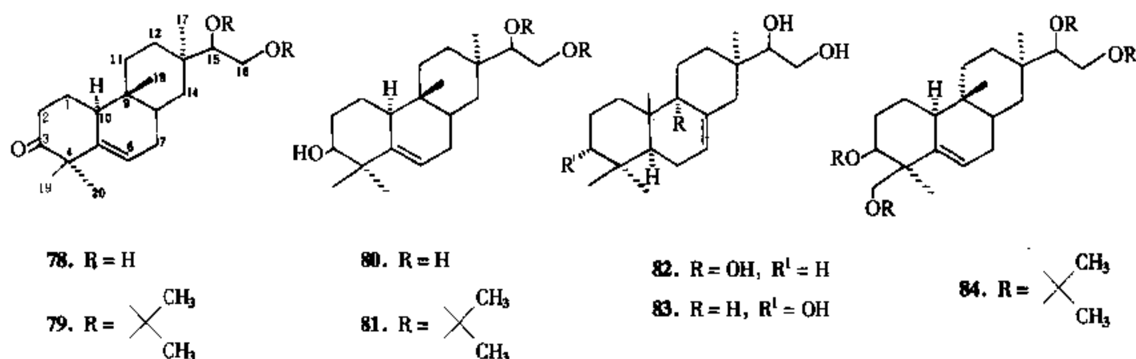
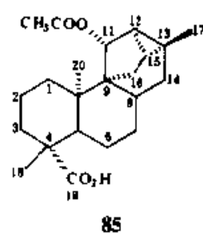
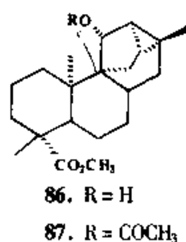


表 9-12　海松烷衍生物 85～89 的¹H-NMR 化学位移[20,21]

质子 \ 化合物	85	86	87	88	89
1-H	—	—	—	—	6.31d(7)
3-H_α	2.17bd	2.23bd	2.21ddd	2.15ddd	—
3-H_β	0.95m	0.97ddd	0.97ddd	1.08ddd	—
6-H	—	—	—	—	3.43m
10-H	—	—	—	—	2.54d(7)
11-H	4.85bs	3.86bs	4.88bs	5.78d	—
12-H	1.0m	1.0m	1.0m	5.95dd	—
14-H	1.45m	1.45m	1.45m	4.84ddq	5.83dd(7,7)
15-H_A	}1.0m	1.0m	1.0m	2.63dddd	4.86dd(10,1.6)
15-H_B					4.91dd(17,1.6)
16-H	—	—	—	—	1.09s
17-H	0.87s	0.88s	0.88s	1.72dd	—
18-H	1.18s	1.13s	1.12s	1.24s	3.12s
19-H	—	—	—	—	1.28s
20-H	0.95s	0.81s	0.84s	0.86s	0.72s
OCH_3	—	3.60s	3.60s	3.77s	—

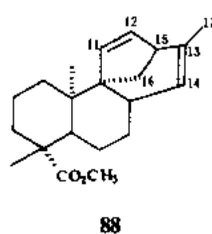


85

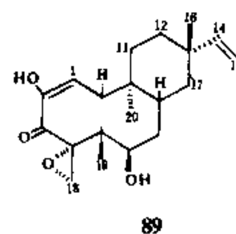


86. R = H

87. R = COCH$_3$



88

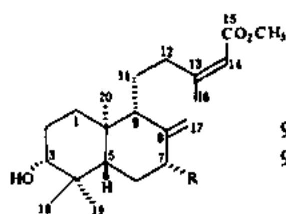


89

四、半日花烷衍生物的^{1}H-NMR化学位移

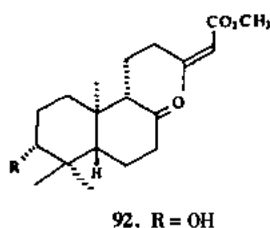
表 9-13　半日花烷衍生物 90 ~ 97 的^{1}H-NMR化学位移[22]

质子 \ 化合物	90	91	92	93	94	95	96	97
1-H	—	—	—	—	—	5.87bs	5.45bs	—
2-H	—	—	—	2.65ddd	2.65ddd	—	4.27m	—
				2.43ddd	2.4m			
3-H$_\alpha$	—	—	—	—	—	2.09d	1.20dd	—
3-H$_\beta$	3.27dd	3.19dd	3.35dd	—	—	2.33d	1.80ddd	—
5-H	—	—	—	—	—	1.8m	1.9m	—
7-H$_\alpha$	2.42ddd	4.38bs	2.1m	2.43bd	—	—	—	—
7-H$_\beta$	1.75m	—	2.85ddd	2.86ddd	—	—	—	—
8-H	—	—	—	—	—	1.55m	1.59m	—
9-H	2.01bdd	—	2.43ddd	2.48ddd	—	—	—	2.44m
12-H	2.56bt	2.58bt	2.05m	2.0m	2.57bt	—	—	—
			2.31ddd	2.35m				
14-H	5.65bs	5.66bs	5.66bs	5.67bs	5.66bs	5.56q	5.66q	5.29t(6)
16-H	1.89d	1.90d	1.91d	1.91d	1.88d	2.16d	2.17d	1.65s
17-H$_A$	4.40bs	5.07bs	—	—	2.91d	}0.84d	0.85d	4.86s
17-H$_B$	4.67bs	4.96bs	—	—	2.43d			4.93s
18-H	1.00s	1.11s	1.09s	1.19s	1.12s	1.02s	1.00s	1.02s
19-H	0.78s	1.17s	0.82s	1.08s	1.09s	1.04s	1.03s	9.70s
20-H	0.69s	0.98s	0.72s	0.93s	1.06s	0.99s	0.85s	0.57s
OCH$_3$	3.67s	3.67s	3.66s	3.66s	3.67s	3.70s	3.69s	—

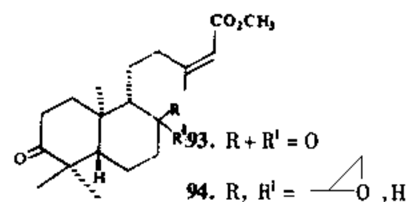


90. R = H

91. R = OH

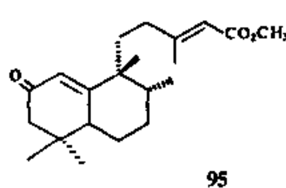


92. R = OH

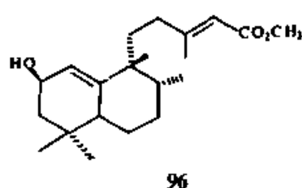


93. R + R^1 = O

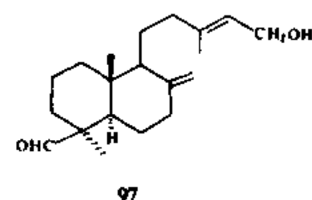
94. R, R^1 = epoxide, H



95



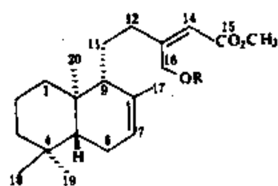
96



97

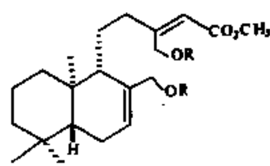
表 9-14 半日花烷衍生物 99～107 的 ^1H-NMR 化学位移[23]

质子 \ 化合物	99	100	101	102	103	104	105	106	107
6-H	1.93m	1.9m	1.92m	2.0m	2.41m 2.28m	2.38m 2.28m	1.95m	—	—
7-H	5.42bs	5.42bs	5.75bd	5.82bd	6.88ddt	6.83ddt	5.70bd	5.77bd	5.84m
9-H	1.93m	1.9m	2.08m	2.0m	2.1m	2.05m	1.95m	—	—
12-H_A	2.69ddd	2.73ddd	2.94ddd	2.71ddd	3.01ddd	2.95ddd	3.09ddd	—	—
12-H_B	2.54ddd	2.58ddd	2.43ddd	2.56ddd	2.61ddd	2.67dd	2.32ddd	—	—
14-H	5.97t	5.83t	5.94t	5.82t	5.86t	5.79t	5.84t	5.82bs	5.56bt
15-H	—	—	—	—	—	—	—	—	4.69bd
16-H_A	4.23d	4.64d	4.26dd	4.62bs	4.29bd	4.78d	4.65d	4.64t	4.63bd
16-H_B			4.13dd		4.21bd	4.69d			4.68bd
17-H_A	1.78bs	1.76bs	4.32bd	4.68bd	9.37s	9.40s	4.34bd	4.06bd	4.47bd
17-H_B			4.02bd	4.54bd			4.01bd	3.70bd	4.57bd
18-H	0.85s	0.87s	0.89s	0.89s	0.94s	0.94s	0.89s	0.90s	0.89s
19-H	0.86s	0.85s	0.87s	0.87s	0.90s	0.89s	0.87s	0.88s	0.87s
20-H	0.74s	0.79s	0.79s	0.76s	0.81s	0.82s	0.75s	0.76s	0.77s
OCH_3	3.72s	3.72s	3.72s	3.71s	3.72s	3.73s	3.72s	3.72s 3.30s	—
$OCOCH_3$	—	2.12s	—	2.13s	—	2.13s	2.13s	2.13s	2.06s 2.07s



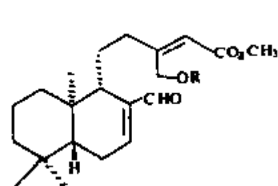
99. R = H

100. R = $COCH_3$



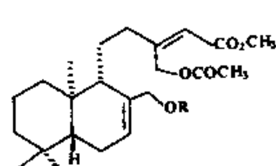
101. R = H

102. R = $COCH_3$



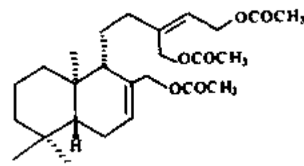
103. R = H

104. R = $COCH_3$



105. R = H

106. R = CH_3



107

表 9-15 半日花烷衍生物 108 ~ 114 的^{1}H-NMR 化学位移[24~26]

质子 \ 化合物	108	109	110	111	112	113	114
1-H	4.81dd	3.57dd	—	—	—	—	—
5-H	—	—	—	—	—	—	1.62d
7-H	—	—	1.92m	—	1.95m	1.95m	—
8-H	—	—	1.80dq	—	1.7m	1.79m	—
11-H_A	2.46ddd	2.41ddd	2.37m	2.37m	2.36m	2.32dd	2.50dd
11-H_B	2.20ddd	2.20ddd	2.37m	2.37m	2.36m	2.45dd	2.42dd
12-H	5.58bt	5.58bt	5.64bt	5.67bt	5.67bt	5.67bt	5.61bs
14-H	6.33dd	6.35dd	4.16m	4.29m	4.83m	4.53t	6.41dd
15-H_A	4.91bd	4.93bd	3.61m	4.14m	4.19m	3.62dd	4.97bd
15-H_B	5.07bd	5.08bd	3.61m	4.14m	4.19m	4.05dd	5.12bd
16-H	1.77bs	1.80bs	1.66bs	1.70bs	1.71bs 1.69bs	1.68bs	1.78bs
17-H	1.19s	1.18bs	1.05d	1.06d	1.05d 1.04d	1.07d	1.07dd
18-H_A	3.92d	3.45d	}0.99s	0.99s	0.90s	0.90s	3.43d
18-H_B	3.85d	3.12d					3.13d
19-H	0.93s	0.91s	0.94s	0.94s	0.85s	0.86s	1.08s
20-H	0.85s	0.77s	1.03s	1.04s	1.03s	1.04s	0.80s
CH_3	—	—	—	—	—	1.47s	—
CH_3	—	—	—	—	—	1.40s	—

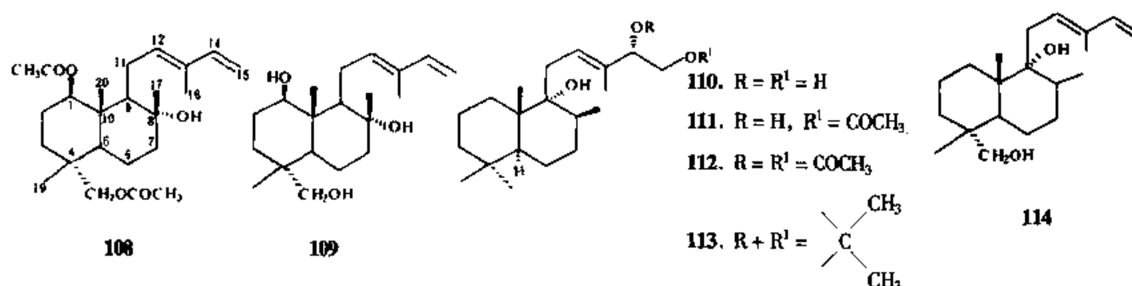
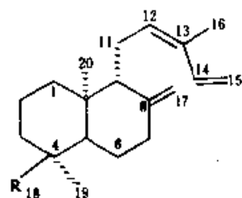
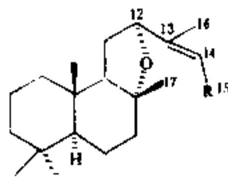


表 9-16 半日花烷衍生物 115 ~ 121 的^{1}H-NMR 化学位移[18,23]

质子 \ 化合物	115	116	117	118	119	120	121
12-H	5.33bt	5.31bt	5.32bt	5.41bt	4.33dd	4.34bdd	4.41bdd
14-H	6.81dd	6.79ddd	6.80ddd	6.33dd	5.79tdq	5.73tdq	6.13dq
15-H_C	5.09bd	5.10bd	5.09bd	4.88bd	}4.19bd	}4.65bd	—
15-H_t	5.18bd	5.20bd	5.18bd	5.04bd			
16-H	1.78dt	1.78d	1.77dt	1.75dt	1.67bs	1.68bs	2.10d
17-H_A	4.83ddd	4.86ddd	4.83ddd	4.82ddd	}1.14s	1.12s	1.13s
17-H_B	4.48ddd	4.53ddd	4.49ddd	4.48ddd			
18-H	0.89s	9.24s	3.42d 3.11d	—	0.83s	0.88s	0.88s
19-H	0.83s	1.06s	}0.77	1.16s	0.82s	0.83s	0.83s
20-H	0.74s	0.79s		0.76s	0.88s	0.83s	0.83s
OCH_3	—	—	—	3.66s	—	—	3.69s



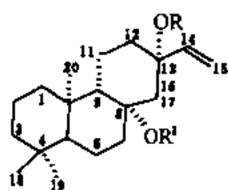
115. R = CH_3
116. R = CHO
117. R = CH_2OH
118. R = CO_2CH_3



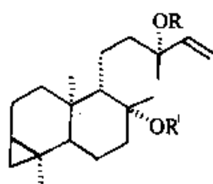
119. R = CH_2OH
120. R = CH_2OCH_3
121. R = CO_2CH_3

表 9-17 半日花烷衍生物 122～131 的 ^{1}H-NMR 化学位移[27,28]

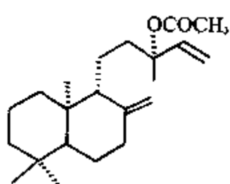
质子＼化合物	122	123	124	125	126	127	128	129	130	131
3-H	—	—	0.56ddd	0.56ddd	—	0.57ddd	—	—	—	—
7-H	—	—	—	—	—	—	5.58bd	5.77bq	5.61bs	5.79bs
14-H	5.88dd	5.96dd	5.89dd	5.97dd	5.95dd	5.98dd	5.43tq	5.46tq	5.90bd	5.93bd
15-H_t	5.23bd	5.15bd	5.24dd	5.16bd	5.13dd	5.13bd	4.16bd	4.19bd	10.00d	10.02d
15-H_C	5.07bd	5.11bd	5.08dd	5.12bd	5.10dd	5.12bd				
16-H	1.25s	1.52s	1.26s	1.5s	1.54s	1.55s	1.70bs	1.72bs	2.19d	2.22d
17-H	1.15s	1.44s	1.22s	1.52s	4.80ddd	4.86ddd	1.77bs	1.94dd	1.77bs	1.94bs
					4.49ddd	4.55ddd				
18-H_A	0.86s	0.85s	0.45dd	0.45dd	0.87s	0.93s	1.05s	1.16s	1.05s	1.17s
18-H_B			0.01dd	0.01dd						
19-H	0.78s	0.71s	0.96s	0.94s	0.81s	0.80s	1.31s	1.14s	1.31s	1.14s
20-H	0.76s	0.81s	0.78s	0.84s	0.68s	0.65s	1.03s	0.85bs	1.04s	0.87s
$OCOCH_3$	—	1.99s	—	2.00s	2.02s	2.02s	—	—	—	—
		1.94s		1.95s						



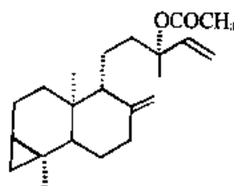
122. R = R^1 = H
123. R = R^1 = $COCH_3$



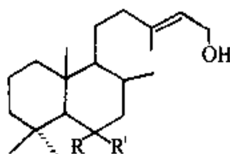
124. R = R^1 = H
125. R = R^1 = $COCH_3$



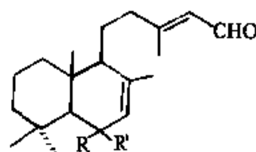
126



127



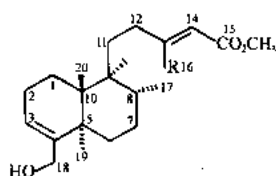
128. R = OH, R^1 = H
129. R = H, R^1 = OH

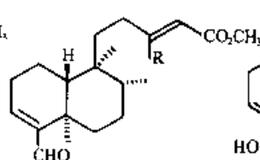


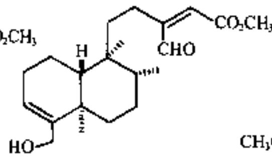
130. R = OH, R^1 = H
131. R = H, R^1 = OH

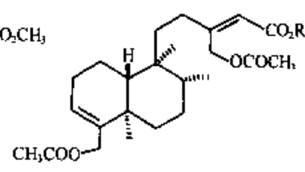
表 9-18 半日花烷衍生物 132～139 的^{1}H-NMR 化学位移[23]

质子＼化合物	132	133	134	135	136	137	138	139
2-H	—	—	2.50m	2.57m	2.57m	—	—	—
3-H	5.57bt	5.58bt	6.61bt	6.61bt	6.63bt	—	5.60bt	5.60bt
8-H	—	—	1.50m	—	—	—	—	1.58m
11-H	—	—	1.50m	—	—	—	—	1.68m
12-H$_A$	}2.45m	2.43ddd	2.54m	—	2.6m	—	}2.45m	2.48ddd
12-H$_B$		2.34ddd	2.32ddd	—	2.47ddd	—		2.41dd
14-H	5.81t	5.95t	5.84t	5.96t	6.45s	6.45s	5.81t	4.59d
16-H	4.59d	4.17d	4.61d	4.15d	9.52s	9.51s	4.62d	4.59d
17-H	0.86d	0.86d	0.87d	0.85d	0.88d	0.86d	0.87d	0.87d
18-H	4.08bs	4.09bs	9.31s	9.29s	9.32s	4.13bs	4.52bs	4.52bs
19-H	1.07s	1.08s	1.16s	1.16s	1.17s	1.08s	1.08s	1.08s
20-H	0.73s	0.73s	0.75s	0.79s	0.71s	0.71s	0.74s	0.74s
OCH$_3$	3.70s	3.71s	3.71s	3.71s	3.83s	3.69s	—	3.71s
COCH$_3$	2.13s	—	2.13s	—	—	—	2.15s 2.07s	2.13s 2.07s









132. R = CH_2OCOCH_3
133. R = CH_2OH

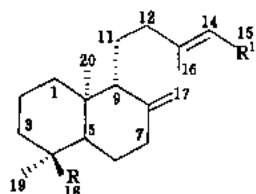
134. R = CH_2OCOCH_3
135. R = CH_2OH
136. R = CHO

137

138. R = H
139. R = CH_3

表 9-19 半日花烷衍生物 140～147 的^{1}H-NMR 化学位移[29]

质子＼化合物	140	141	142	143	144	145	146	147
14-H	3.37bt(7)	5.39bt(7)	5.33bt(7)	5.32bt(7.5)	5.89bd(8)	5.88bd(8)	5.40bt(7)	5.33bt(7)
15-H	4.16d(7)	4.15d(7)	4.60d(7)	4.59d(7.5)	10.99d(8)	10.00d(8)	4.16d(7)	4.57d(7)
16-H	1.67bs	1.67bs	1.71bs	1.70bs	2.17d(1)	2.17d(1)	1.67bs	1.70bs
17-H$_A$	4.86bs	4.83bs	4.85bs	4.84bs	4.87bs	4.86bs	4.84bs	4.84bs
17-H$_B$	4.54bs	4.53bs	4.54bs	4.53bs	4.51bs	4.50bs	4.53bs	4.53bs
18-H$_A$	—	—	—	—	—	—	3.10d	3.63d
18-H$_B$	—	—	—	—	—	—	3.44d	3.87d
19-H	1.15s	1.14s	1.16s	1.14s	1.15s	1.14s	0.76s	0.82s
20-H	0.72s	0.70s	0.73s	0.71s	0.73s	0.71s	0.72s	0.72s
OCH$_3$	—	3.65s	—	3.67s	—	3.66s	—	—
CO$_2$H	3.70m	—	—	—	4.23m	—	—	—
OCOCH$_3$	—	—	2.07s	2.07s	—	—	—	2.05s



140. R = CO_2H, R^1 = CH_2OH

141. R = CO_2CH_3, R^1 = CH_2OH

142. R = CO_2H, R^1 = CH_2OCOCH_3

143. R = CO_2CH_3, R^1 = CH_2OCOCH_3

144. R = CO_2H, R^1 = CHO

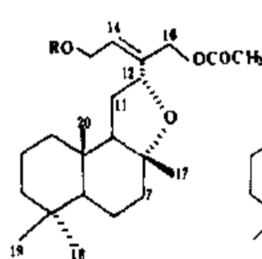
145. R = CO_2CH_3, R^1 = CHO

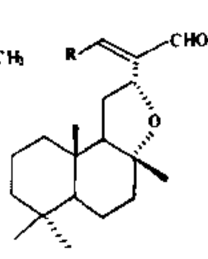
146. R = R^1 = CH_2OH

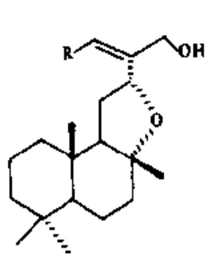
147. R = R^1 = CH_2OCOCH_3

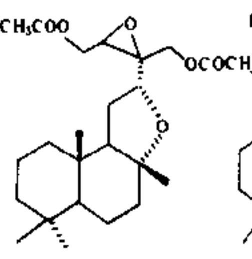
表 9-20 半日花烷衍生物 148～156 的^{1}H-NMR 化学位移[30]

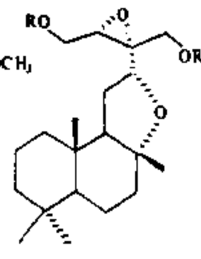
质子 \ 化合物	148	149	150	151	152	153	154	155	156
7-H_β	1.97ddd	1.96ddd	2.01ddd	1.98ddd	1.97ddd	1.98ddd	—	—	—
12-H	4.80dd	4.79dd	5.00dd	5.0m	4.86dd	5.33dd	4.10dd	4.10dd	4.07dd
14-H	5.66bt	5.81bt	6.38dd	6.59dd	5.73bt	6.12bt	3.34dd	3.34dd	3.26dd
15-H_A	4.7m	4.22m	10.84	5.25m	4.27dd	10.15d	4.37d	3.89m	4.50dd
15-H_B					4.11dd		4.09d		4.36dd
16-H_A	4.7m	4.58d	9.62s	9.35s	3.99dd	4.52d	4.39d	4.10dd	4.37d
16-H_B		4.72d			4.37d	4.22d	4.44d	3.64dd	4.06d
17-H	1.19s	1.18s	1.17s	1.15s	1.25s	1.21s	1.17s	1.19s	1.17s
18-H	0.83s	0.83s	0.82s	0.82s	0.84s	0.82s	0.83s	0.82s	0.82s
19-H	0.86s	0.85s	0.83s	0.82s	0.87s	0.82s	0.86s	0.86s	0.86s
20-H	0.89s	0.87s	0.88s	0.88s	0.88s	0.89s	0.88s	0.88s	0.88s
$COCH_3$	2.07s	2.08s	—	—	—	—	2.07s	—	2.07s
	2.10s	—	—	—	—	—	2.11s	—	2.11s
OH	—	2.35bs	—	—	2.16bs	—	—	—	—











148. R = $COCH_3$ **149.** R = H

150. R = CHO **151.** R = CH_2OH

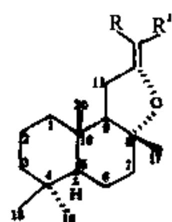
152. R = CH_2OH **153.** R = CHO

154

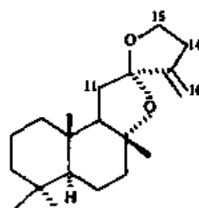
155. R = H **156.** R = $COCH_3$

表 9-21 半日花烷衍生物 157～163 的^{1}H-NMR 化学位移[30]

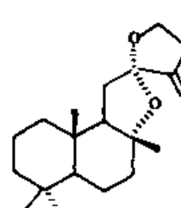
质子 \ 化合物	157	158	159	160	161	162	163
6-$H_α$	1.38dddd	—	1.37dddd	1.38dddd	—	—	—
6-$H_β$	1.91dddd	—	1.90dddd	1.90dddd	—	—	—
7-$H_α$	2.14ddd	—	2.12ddd	2.12ddd	—	—	—
7-$H_β$	1.66ddd	—	1.6m	1.65m	—	—	—
9-H	1.75dd	—	1.73dd	1.79dd	1.63dd	1.83dd	—
11-H_A	2.50d	2.38dd	2.70dd	3.11dd	2.10dd	2.04dd	2.87dd
11-H_B		2.23dd	2.50dd	2.73dd	2.01dd	1.96dd	2.65dd
14-H_A	3.16dd	2.26m	2.39t	3.28bd	2.61m	2.75m	—
14-H_B	3.27dd			3.37bd		2.59m	—
15-H	9.53dd	3.67t	3.64bt	9.54dd	3.91m	3.98dd 5.10dd	4.73s
16-H_A	10.04s	4.13d	10.03s	9.71s	5.12dd	5.17dd	4.73s
16-H_B		4.12d			5.04dd	5.10dd	
17-H	1.28s	1.14s	1.26s	1.30s	1.20s	1.25s	1.28s
18-H	0.85s	0.84s	0.86s	0.84s	0.87s	0.86s	0.85s
19-H	0.91s	0.86s	0.91s	0.90s	0.89s	0.89s	0.91s
20-H	0.91s	0.87s	0.91s	0.93s	0.89s	0.89s	0.91s



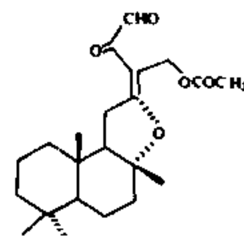
157. R = CH_2CHO, R^1 = CHO
158. R = CH_2CH_2OH, R^1 = CH_2OH
159. R = CH_2CH_2OH, R^1 = CHO
160. R = CHO, R^1 = CH_2CHO



161



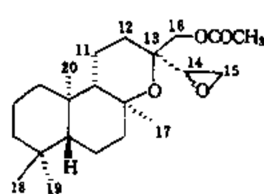
162



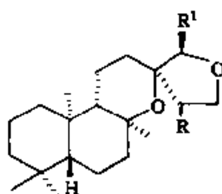
163

表 9-22 半日花烷衍生物 164～169 的^{1}H-NMR 化学位移[31]

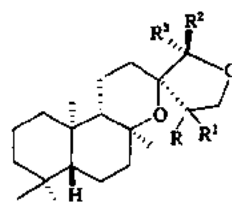
质子 \ 化合物	164	165	166	167	168	169
14-H	3.04dd	3.79ddd	3.91ddd	4.98dd	4.13dd	—
15-H_A	2.83d	4.03dd	4.15d	4.29dd	4.29dd	4.12s
15-H_B		3.90dd		3.99dd	4.24dd	
16-H_A	4.05d	4.88d	5.91s	5.93s	—	6.32s
16-H_B	3.90d					
17-H	1.26s	1.37s	1.34s	1.15s	1.34s	4.37s
18-H	0.87s	0.88s	0.86s	0.85s	0.88s	0.87s
19-H	0.80s	0.81s	0.79s	0.79s	0.80s	0.82s
20-H	0.76s	0.81s	0.78s	0.76s	0.79s	0.81s
$COCH_3$	2.11s	—	2.07s	2.11s 2.09s	—	2.18s
OH	—	2.92s	3.06s	—	3.00bs	—



164



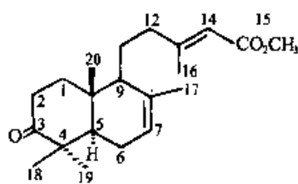
165. R = OH, R¹ = OH
166. R = OH, R¹ = OCOCH$_3$
167. R = OCOCH$_3$, R¹ = OCOCH$_3$



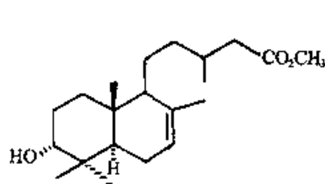
168. R, R¹ = OH, H R² + R³ = O
169. R + R¹ = O, R² = OCOCH$_3$, R³ = H

表 9-23 半日花烷衍生物 170～176 的^{1}H-NMR 化学位移[32,33]

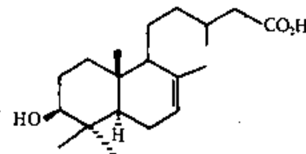
质子 \ 化合物	170	171	172	173	174	175	176
2-H	2.73ddd 2.37m	—	—	—	—	2.15m	2.15m
3-H	—	3.24dd	3.45bs	3.24dd	3.45bs	5.60m	5.58m
7-H	5.46m	5.43m	5.40m	5.43m	5.40m	—	—
12-H$_A$	—	—	—	—	—	2.24ddd	2.24ddd
12-H$_B$	—	—	—	—	—	2.32ddd	2.30ddd
14-H	5.68q	5.68bs	5.66bs	—	2.39d 2.16d	6.24dt	6.26dt
15-H	—	—	—	—	—	7.34dd	7.35dd
16-H	2.19d	2.18d	2.19d	0.97d	1.00d	7.19bs	7.20bs
17-H	1.73bs	1.70bs	1.70bs	1.66bs	1.67bs	0.84d	0.84d
18-H	1.11s	0.98s	0.98s	0.98s	0.98s	1.08s	1.09s
19-H	1.09s	0.87s	0.87s	0.87s	0.91s	4.60bs	4.10bs
20-H	1.01s	0.77s	0.77s	0.77s	0.78s	0.75s	0.75s
OCH$_3$	3.71s	3.69s	3.69s	3.66s	—	3.75s	—



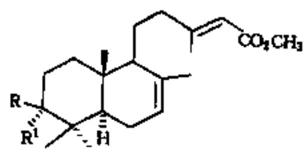
170



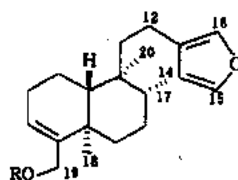
173



174



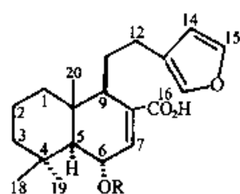
171. R = H, R¹ = OH
172. R = OH, R¹ = H

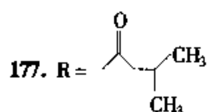


175. R = COCH$_3$
176. R = H

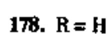
表 9-24 半日花烷衍生物 177 ~ 186 的 ^{1}H-NMR 化学位移[34,35]

质子 \ 化合物	177	178	179	180	181	182	183	184	185	186
3-H	—	—	—	—	—	—	—	—	4.58dd	—
5-H	—	1.20d	2.12s	—	—	—	—	—	—	—
6-H	5.65bd	4.42bd	—	4.29bd	3.88m	3.93m	—	—	—	—
7-H	6.47bs	6.71bs	6.29d	5.70bs	—	—	2.41ddd	2.40ddd	—	2.41ddd
9-H	2.19m	2.15m	2.55m	1.95m	—	—	—	—	—	—
11-H_A	1.75m	1.7m	1.78m	1.67m	—	—	—	—	—	—
11-H_B	1.5m	1.45m	1.5m	1.45m	—	—	—	—	—	—
12-H_A	2.78ddd	2.78ddd	2.78ddd	2.67ddd	}2.32m	2.37m	2.56ddd	2.55ddd	}2.52m	3.83m
12-H_B	2.37m	2.40ddd	2.46ddd	2.42ddd			2.25ddd	2.24ddd		
14-H	6.25bs	6.25bs	6.26bs	6.27bs	6.21bs	6.27bs	6.27bs	6.26bs	6.30bs	5.58t
15-H	7.32bs	7.32bs	7.35dd	7.35dd	7.33dd	7.35dd	7.34dd	7.34dd	7.35dd	—
16-H	7.19bs	7.20bs	7.23bs	7.22bs	7.17bs	7.21bs	7.20bs	7.20bs	7.25bs	4.86bs
17-H	—	—	—	4.21bd	—	3.75bd	4.87bs	4.87bs	1.16s	4.56bs
				4.09bd		3.57bd	4.58bs	4.57bs		4.54bs
18-H	0.99s	1.15s	1.18s	1.15s	1.16s	1.14s	0.98s	0.75s	0.91s	0.99s
19-H_A	—	1.08s	1.11s	1.06s	1.02s	1.04s	3.76d	3.41d	}0.89s	3.76d
19-H_B	—	—	—	—	—	—	3.40bd	3.11bd		3.41bs
20-H	0.93s	0.88s	0.92s	0.81s	0.84s	0.85s	0.67s	0.73s	0.86s	0.68s
OCH_3	—	—	3.81s	—	3.68s	—	—	—	—	—

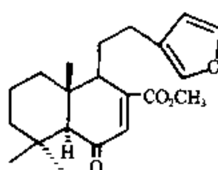




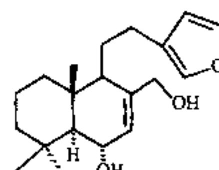
177. R =



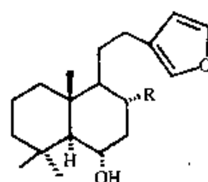
178. R = H



179

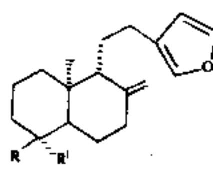


180



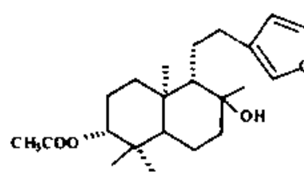
181. R = CO_2CH_3

182. R = CH_2OH

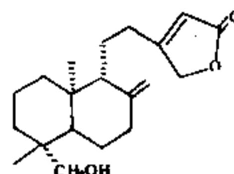


183. R = CH_3, R^1 = CH_2OH

184. R = CH_2OH, R^1 = CH_3



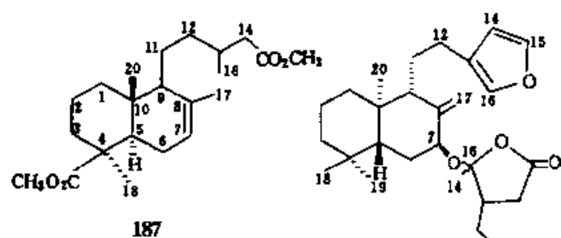
185



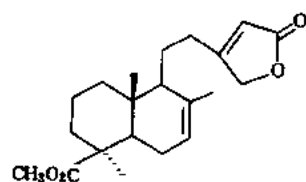
186

表 9-25　半日花烷衍生物 187～194 的^{1}H-NMR 化学位移[23,34,36～38]

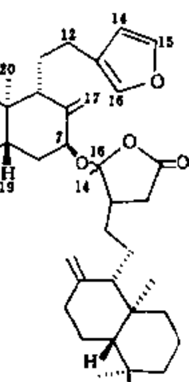
质子＼化合物	187	188	189	190	191	192	193	194
1-H	1.06ddd	1.07ddd	—	—	—	—	5.42dt	1.88d
2-H	—	—	—	—	2.5m 2.34m	2.50m 2.35m	5.94bd	—
3-H	2.16bd 1.01ddd	2.16bd 1.02ddd	—	—	6.86dd	6.72dd	7.42dd	6.01qq
5-H	1.41dd	1.42dd	—	—	—	—	—	5.90dq
6-H	2.16m 1.90bd	2.18m 1.89m	—	—	2.70d 2.36bd	2.0m 2.35dd	2.12t(13) 2.70d(13)	—
7-H	5.42bd	5.47bd	4.35dd	4.25dd	—	4.11ddd	1.3～1.7m	2.45bdd
8-H	—	—	—	—	2.58q	—	1.3～1.7m	2.0m
9-H	—	—	—	—	—	—	—	2.2m
10-H	—	—	—	—	—	—	1.86d(13) 2.25t(13)	5.67bd
11-H	1.5～1.7m	1.53～1.72m	—	—	—	—	1.3～1.7m	—
12-H	2.37m	2.62ddd 2.40ddd	2.75m 2.3m	2.75m 2.3m	—	—	2.42t(9)	3.33bd
13-H	—	—	—	—	2.87m	2.50m	—	—
14-H	5.66bs	5.86dt	6.27bs	6.30bs	2.21ddd 2.71dd	2.19ddd 2.70dd	6.28bs	6.05qq
15-H	—	—	7.36bs	7.33bs	—	—	7.23bs	—
16-H	2.18d	4.77bs	7.19bs	7.23bs	3.97ddd 4.48dd	3.94ddd 4.47dd	7.37t	1.83d
17-H	1.70bs	1.70bs	5.21bs 4.92bs	5.11bs 4.77bs	0.99d	1.04d	0.80d(6)	2.01d
18-H	0.63s	0.65s	0.88s	0.88s	0.64s	0.87s	4.87s 5.12bs	1.63bs
19-H	—	—	0.82s	0.87s	3.92dd 4.01d	3.91dd 5.30d	—	2.23d
20-H	1.19s	1.20s	0.72s	0.72s	—	—	0.73s	2.14d

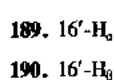


187



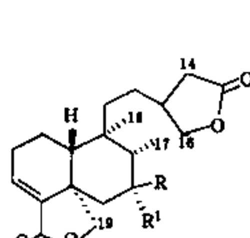
188

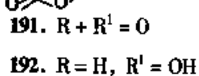




189. 16′-H_α

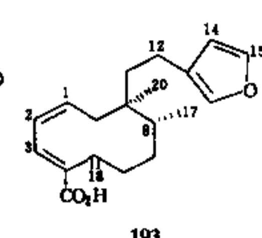
190. 16′-H_β



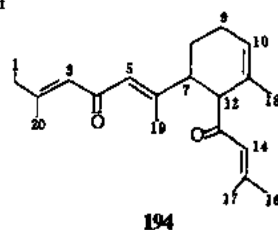


191. R + R^1 = O

192. R = H, R^1 = OH



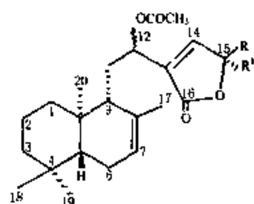
193

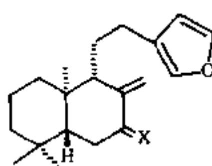


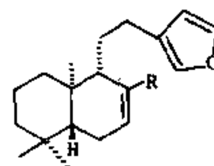
194

表 9-26 半日花烷衍生物 195 ~ 200 的^{1}H-NMR 化学位移[23]

质子 \ 化合物	195	196	197	198	199	200
6-H$_A$	—	—	—	2.61dd	—	—
6-H$_B$	—	—	—	2.31dd	—	—
7-H	5.49bs	5.49bs	4.39bs	—	5.78bs	6.83ddd
12-H$_A$	} 5.71dt	5.70dt	2.54ddd	2.58ddd	2.72ddd	2.90ddd
12-H$_B$			2.26ddd	2.30m	2.45ddd	2.40m
14-H	7.00d	7.06d	6.28dd	6.27bs	6.30bs	6.34bs
15-H	6.09t	6.18t	7.35dd	7.36dd	7.36dd	7.34dd
16-H	—	—	7.21dd	7.22bs	7.21bs	7.23bs
17-H$_A$	} 1.71bs	1.71bs	5.01dd	5.87dd	4.20bd	} 9.42s
17-H$_B$			4.70dd	5.16dd	4.02bd	
18-H	0.89s	0.89s	0.89s	0.88s	0.89s	0.94s
19-H	0.87s	0.87s	0.89s	0.88s	0.87s	0.90s
20-H	0.78s	0.80s	0.68s	0.84s	0.76s	0.81s
COCH$_3$	2.19s	2.16s	—	—	—	—
	2.13s	2.08s	—	—	—	—





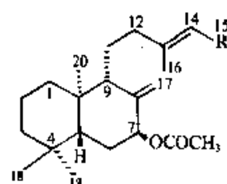


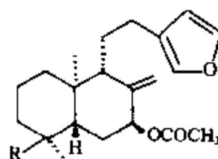
195. R = OCOCH$_3$, R^1 = H　**197**. X = β-OH, α-H　**199**. R = CH$_2$OH

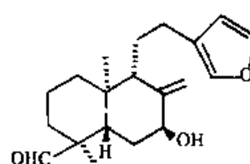
196. R = H, R^1 = OCOCH$_3$　**198**. X = O　**200**. R = CHO

表 9-27 半日花烷衍生物 201 ~ 207 的^{1}H-NMR 化学位移[39]

质子 \ 化合物	201	202	203	204	205	206	207
7-H	5.41t	5.41t	5.41t	5.36t	5.39t	5.38t	4.36t
12-H$_A$	—	} 2.3m	2.51bddd	2.53bddd	2.52bddd	2.51ddd	2.56ddd
12-H$_B$	—		2.26bddd	2.25bddd	2.66bddd	2.27ddd	2.28ddd
14-H	5.37bt	5.84bd	6.25bs	6.25bs	6.26bs	6.25bs	6.28bs
15-H	4.15bd	10.0d	7.35dd	7.36dd	7.36dd	7.36dd	7.36dd
16-H	1.68bs	2.16bs	7.17bs	7.17bs	7.17bs	7.17bs	7.22bs
17-H$_A$	5.18bs	5.21bs	5.22bs	5.26bs	5.24bs	5.23bs	5.11bs
17-H$_B$	4.76bs	4.73bs	4.81bs	4.86bs	4.82bs	4.82bs	4.74bs
18-H	0.84s	0.83s	0.83s	9.19s	3.83d	3.35d	9.24s
					3.59d	3.06d	
19-H	0.80s	0.79s	0.80s	1.03s	0.82s	0.74s	1.04s
20-H	0.69s	0.69s	0.69s	0.75s	0.72s	0.74s	0.74s
COCH$_3$	2.05s	2.04s	2.04s	2.05s	2.07s	2.02s	—







201. R = CH_2OH
202. R = CHO

203. R = CH_3
204. R = CHO
205. R = CH_2OCOCH_3
206. R = CH_2OH

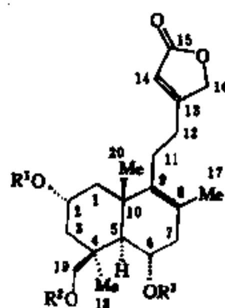
207

表 9-28 半日花烷衍生物 208～215 的^{1}H-NMR 化学位移[69]

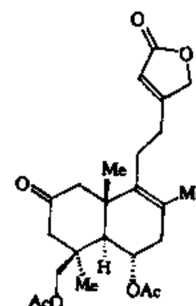
质子 \ 化合物	208	209	210	211
1α-H	1.49dd(t) (11.4,11.4)	1.16dd(t) (11.6,11.6)	1.20dd(t) (11.5,11.5)	1.19dd(t) (11.6,11.6)
1β-H	2.42hm	2.12hm	2.13dd (12.4,3.5)	2.15ddd (11.7,3.7,2.1)
2-H	4.27dddd (11.4,11.4,3.9,3.9)	3.91dddd (11.5,11.5,4.0,4.0)	3.92dddd (11.5,11.5,3.9,3.9)	3.94dddd (11.4,11.4,3.8,3.8)
3-H	1.54αdd(t) (12.1,12.1) 2.35hm	1.10αdd(t) (12.9,12.9) 1.96βddd (13.2,3.9,2.1)	1.01αdd(t) (12.4,12.4) 2.13βdd (12.4,3.5)	1.10αdd(t) (12.5,12.5) 1.95βddd (13.2,3.6,1.9)
5-H	1.66d (11.1)	1.45d (11.2)	1.69d (11.9)	1.70d (11.9)
6-H	4.61ddd (10.3,10.3,6.3)	4.15ddd (10.9,9.8,6.1)	5.25ddd (11.8,8.5,6.7)	5.23ddd (11.9,8.8,6.4)
7-H	2.40αhm[dd] (17.4,10.2)	2.11αhm[dd] (17.0,9.4) 2.39βdd (17.5,6.1)	2.01αdd (17.6,8.8)	2.01αdd (17.4,8.5) 2.57βdd (17.3,6.4)
11-H	2.20m 2.30m	2.17m 2.33m	2.20m 2.35m	2.20m 2.35m
12-H	2.35(2H)m	2.43(2H)m	2.43(2H)m	2.43(2H)m
14-H	5.97m(5pk) (1.5)	5.87m(5pk) (1.3)	5.88m(5pk) (1.4)	5.87m(5pk) (1.3)
16-H	4.71dd (17.3,1.7) 4.75dd (17.3,1.5)	4.74d (1.5)	4.75d (1.7)	4.75d (1.7)
17-H	1.57s	1.61s	1.58s	1.58s
18-H	1.74s	1.32s	1.22s	1.23s
19-H	3.84d (10.4) 4.49d (10.5)	4.17d (11.1) 4.38d (11.2)	3.56d (10.8) 3.69d (10.8)	4.07d (11.4) 4.13d (11.4)
20-H	1.27s	1.06s	1.10s	1.10s
Misc.	5.59brs 6-OH 5.89brs 2-OH 6.83brs 19-OH	2.09s 19-Ac	2.07s 6-Ac	2.08s 6-Ac 2.04s 19-Ac

续表

质子 \ 化合物	212	213	214	215
1α-H	1.26dd(t) (11.4,11.4)	2.24d (15.5)	1.23dd (12.2,12.2)	1.24dd (11.5,11.5)
1β-H	2.02hm (11.4,3.6,2.2)	2.52d (15,4)	2.05ddd (11.4,3.6,2.2)	2.08hm [ddd](11,4.5,2.2)
2-H	4.99dddd (11.7,11.7,4.0,4.0)		4.93dddd (11.8,11.8,4.0,4.0)	4.98dddd (11.8,11.8,4.1,4.1)
3-H	1.17αdd(t) (12.8,12.8)	2.16αd (15.2) 2.69βd (15.2)	1.23αdd (12.9,12.2) 1.73βddd (13.2,4.0,2.0)	1.18αdd (12.6,12.6) 2.02βddd (10.9,4.1,2.1)
5-H	1.72d (11.8)	2.04hd (11)	1.41d (11.0)	1.47d (11.2)
6-H	5.23ddd (11.8,8.7,6.5)	5.18ddd (11.9,9.0,6.2)	4.27ddd (10.5,10.5,5.9)	4.16ddd (11.1,9.6,6.0)
7-H	2.00αhm[dd] (17.6,8.7) 2.58βdd (17.3,6.4)	2.03αhdd (17.4,8.3) 2.62βdd (17.3,6.2)	2.12αdd (17.1,10.4) 2.32βdd (17.6,5.6)	2.11hm[dd] (17,9.5) 2.40hm[dd] (17.0,7.1)
11-H	2.18m 2.33m	2.15m 2.28m	2.14m 2.32m	2.16m 2.32m
12-H	2.40(2H)m	2.41(2H)m	2.42(2H)m (8.2)	2.40(2H)m
14-H	5.87m(5pk) (1.3)	5.86m(5pk) (1.5)	5.87m(5pk) (1.5)	5.86m(5pk) (1.6)
16-H	4.75s	4.73d (1.6)	4.75d (1.6)	4.74d (1.7)
17-H	1.58s	1.60s	1.62s	1.61s
18-H	1.22s	1.25s	1.34s	1.31s
19-H	4.07d (11.5) 4.18d (11.5)	4.03d (11.3) 4.11d (11.3)	3.47d (10.2) 4.23d (10.4)	4.15d (11.4) 4.45d (11.3)
20-H	1.15s	1.20s	1.18s	1.10s
Misc.	2.03s Ac 2.04s Ac 2.07s Ac	2.04s Ac 2.09s Ac	2.08s Ac	2.03s 2-Ac 2.10s 19-Ac



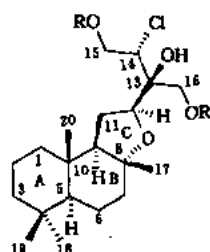
	R^1	R^2	R^3
208.	H	H	H
209.	H	Ac	H
210.	H	H	Ac
211.	H	Ac	Ac
212.	Ac	Ac	Ac
214.	Ac	H	H
215.	Ac	Ac	H



213

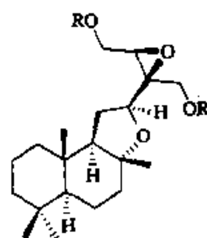
表 9-29 半日花烷衍生物 216 ~ 219 的 ^{1}H-NMR 化学位移[70]

质子 \ 化合物	216	217	218	219
1-H	1.04α ddd (12.8,12.8,3.3)	1.05α ddd (12.9,12.9,3.5)	1.02α ddd (12.8,12.8,3.4)	1.01α ddd (12.9,12.9,3.4)
	1.49β brd (14.0)	1.51β brd (12.9)	1.48β brd (14.1)	1.46β hm
2-H	1.43α hm[brd] (13.8)	1.45α hm	1.41α hm	1.47α hm
	1.68β ddddd (13.2,13.2,13.2, 3.3,3.3)	1.67β hm	1.67β ddddd (14.0,14.0,14.0, 3.7,3.7)	1.66β dddd (13,13,13,3.3)
3-H	1.17α ddd (13.6,13.6,4.2)	1.17α ddd (13.7,13.7,4.6)	1.17α ddd (13.5,13.5,4.0)	1.16α ddd (14.2,14.2,4.6)
	1.42β hm[brd] (12.8)	1.41β hm	1.41β hm[brd] (13.6)	1.41β hm[brd] (14.3)
5-H	0.94dd (12.5,2.7)	0.95dd (12.5,2.7)	0.95dd (12.5,2.7)	0.94dd (12.4,2.6)
6-H	1.78α dddd (13.8,3.3,3.1,3.1)	1.78α dddd (13.8,3.2,3.0,3.0)	1.77α dddd (13.9,3.3,3.3,3.3)	1.76α dddd (13.8,3.1,3.1,3.1)
	1.29β dddd (13.2,13.2,13.2,3.3)	1.28β dddd (13.1,13.1,13.1,3.2)	1.29β dddd (13.2,13.2,13.2,3.3)	1.28β dddd (13.1,13.1,13.1,3.2)
7-H	1.42α hm[ddd] (12.4,12.4,3.7)	1.42α hm	1.44α hm	1.41α hm
	1.91β ddd (11.6,3.1,3.1)	1.92β ddd (11.6,3.1,3.1)	1.93β ddd (11.6,3.1,3.1)	1.93β ddd (11.6,3.2,3.2)
9-H	1.53dd (13.7,4.9)	1.56dd (13.7,4.8)	1.52dd (13.6,5.0)	1.51dd (13.7,5.4)
11-H	1.65α ddd (11.2,5.6,5.6)	1.70α ddd (10.4,5.2,5.2)	1.70α ddd (12.2,5.0,5.0)	1.65α hm
	1.94β ddd (14.0,10.5,10.5)	1.86β ddd (13.6,10.4,10.4)	1.94β ddd (13.6,11.6,10.0)	1.88β ddd (13.6,11.2,9.4)
12-H	4.30dd (9.9,5.8)	4.16dd (9.9,5.8)	4.04dd (9.8,6.2)	4.09dd (9.2,6.8)
14-H	4.08dd (6.3,4.5)	4.23m	3.33dd (6.0,6.0)	3.33dd (7.3,3.5)
15-H	3.79dd (12.3,6.3)	4.23m	3.71dd (12.3,5.8)	4.09dd (12.5,7.2)
	3.97dd (12.4,4.0)	4.58m	3.82dd (12.3,6.0)	4.36dd (12.5,3.6)
16-H	3.64brd (10.9)	4.19d (11.9)	3.82d (12.7)	4.40d (12.6)
	3.99d (11.3)	4.56d (11.8)	3.84d (12.7)	4.42d (12.6)
17-H	1.19s	1.17s	1.19s	1.16s
18-H	0.86s	0.86s	0.86s	0.86s
19-H	0.82s	0.82s	0.82s	0.82s
20-H	0.85s	0.85s	0.86s	0.84s
Misc.	3.23(13-OH)s 2.85(15-OH)brs 3.49(16-OH)brs	2.106(Ac)s 2.110(Ac)s		2.06s 2.10s



216. R = H

217. R = Ac



218. R = H

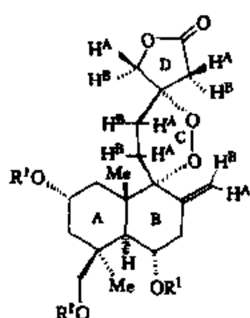
219. R = Ac

表 9.30 半日花烷衍生物 220~228 的 ¹H-NMR 化学位移[?]

位置 \ 化合物	220	221	222	223	224	225	226	227	228
1-H	1.42α dd (11.4,11.4)	1.44α dd (11.4,11.4)	1.32α dd (11.6,11.6)	1.61α dd (11.6,11.6)	1.32α dd (11.4,11.4)	1.30α dd (11.8,11.8)	1.35α dd (11.4,11.4)	1.37α dd (12.0,12.0)	1.67α dd (11.8,11.8)
	1.83β ddd (11.9,4.0,2.3)	1.85β ddd (11.7,3.9,2.0)	1.90β hm	1.85β ddd (11.7,4.2,2.1)	2.72β ddd (11.6,3.6,2.0)	2.23β ddd (11.8,3.7,2.2)	1.88β ddd (11.4,4.1,1.9)	1.75β ddd (12.2,4.0,2.2)	1.83β ddd (12.9,4.7,2.2)
2-H	3.73dddd (11.5,11.5,4.0,4.0,3.9)	3.84dddd (12.5,12.5,3.8,3.8)	4.91hm dddd (11.7,11.7,4.7,4.7)	4.95dddd (11.8,11.8,4.7,4.7)	4.99dddd (11.9,11.9,4.0,4.0)	4.97dddd (11.9,11.9,4.1,4.1)	5.20hm[dddd] (11.6,11.6,4.5,4.4)	4.94dddd (11.9,11.9,4.2,4.2)	4.95dddd (11.8,11.8,4.2,4.3)
3-H	0.97α dd (12.9,12.0)	1.09α dd (12.5,12.5)	1.24α dd (12.8,12.8)	1.25α dd (12.8,12.8)	1.38α dd (12.5,12.5)	1.17α dd (12.6,12.6)	1.20α hm [dd] (11,11)	1.20α dd (12.7,12.7)	1.25α dd (12.6,12.6)
	1.69β ddd (13.0,3.9,2.1)	1.95hm[ddd] (13.1,3.9,2.3)	1.90β hm	1.94β hm	2.04β hm	2.05β hm	2.20β hm [ddd] (11,4.5,2.0)	1.95β hm [ddd] (12.5,4.0,2.2)	1.93β ddd (13.2,3.8,2.1)
5-H	1.98d(11.0)	2.07d(9.5)	2.39d(11.7)	2.44d(11.7)	1.63d(8.7)	1.68d(8.9)	1.51d(11.3)	2.19d(10.4)	2.25d(11.8)
6-H	3.89dddd (11.1,11.1,3.4,4.0)	3.84hm	5.05ddd (11.2,11.2,5.4)	5.03ddd (11.6,10.6,5.2)	5.54hm[dd] (3.3,6.1)	5.46hm,dd (5.9,5.8)	5.28ddd (11.1,9.7,4.7)	5.15ddd (10.3,7.6,4.8)	5.00ddd (11.3,11.3,5.2)
7-H	2.53α dd (11.4,11.4)	2.96α dd (11.8,10.8)	2.50α dd (11.2,11.2)	2.43α dd (11.6,11.6)	1.73α d (15.5)	1.80α d (15.4)	1.70α dd (14.0,9.6)	1.95α dd (16.4,4.7)	2.43α hm [dd] (11.9,11.9)
	2.39β dd (11.8,4.5)	3.32β dd (12.0,5.2)	2.62β dd (12.1,5.2)	2.61β dd (12.4,5.2)	2.84β dd (15.7,6.4)	2.41β dd (15.6,6.2)	2.56β dd (14.1,4.7)	2.31β dd (16.4,7.6)	2.62β dd (12.3,5.1)
11-H	2.00(2H)m	1.96(2H)m	1.90A hm	2.10(2H)hm	5.59(7.5)	5.49t(7.6)	6.08d(15.8)	6.26d(15.8)	2.18A ddd (13.2,7.8,3.2)
			1.99B ddd (14.0,5.0,2.5)						2.05B hm
12-H	2.31A ddd (13.0,9.1,9.5)	2.32A ddd (13.1,12.3,6.5)	2.22A ddd (13.4,13.4,5.2)	2.54(2H)m	3.59(2H)d (7.5)	3.64(2H)m	6.58d(15.8)	6.62d(15.9)	2.43A hm

续表

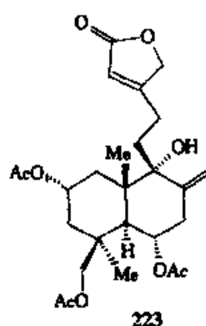
质子 \ 化合物	220	221	222	223	224	225	226	227	228
13-H	1.94 ddd (13.2,2.7,3.1)	1.79 ddd (13.4,4.5,2.9)	1.79 ddd (13.5,4.7,2.0)						1.86 br.s
14-H	2.73 d (18.2) 2.21 d (18.2)	2.48d (18.4) 2.46d (18.4)	2.49d (18.4) 2.44d (18.4)	5.87m(5pk)(1.6)	5.86m(5pk) (1.6)	5.81m(5pk) (1.6)	5.98m(5pk) (1.9)	5.98m(5pk) (1.4)	4.49br.s $w_{1/2}$=4.7Hz
16-H	4.29 d (10.0) 4.10 d (10.0)	4.17d(10.2) 4.94d(10.2)	4.18d(10.2) 4.94d(10.2)	4.73(2H)d (1.8)	4.70(2H)d (1.3)	4.75(2H)d (0.9)	4.91dd (16.4,1.2) 4.96dd (16.4,1.2)	4.95dd (16.3,1.2) 5.00dd (16.5,1.2)	4.14 d (9.0) 4.06 d (9.0)
17-H	5.20 s 4.91 s	5.27 s $w_{1/2}$=2.2Hz 4.86 s $w_{1/2}$=2.7Hz	5.35 d (1.2) 4.89 s	5.12 d (5.3) 4.35 br.m	1.45s	1.49s	1.45s	1.15s	5.04 d (1.7) 4.93 br.m $w_{1/2}$=3.1Hz
18-H	1.28s	1.32s	1.19s	1.21s	1.00s	1.09s	1.25s	1.09s	1.20s
19-H	3.51dd (10.7,4.2) 3.07dd (10.5,4.3)	4.16d(11.0) 4.23d(11.0)	4.06d(11.5) 4.38d(11.5)	4.07d(11.5) 4.40d(11.5)	4.14d(11.4) 4.27d(11.5)	4.13d(11.5) 4.26d(11.5)	3.95d(11.6) 4.12d(11.6)	4.11d(11.5) 4.15d(11.5)	4.08d(11.5) 4.09d(11.5)
20-H	0.95s	0.90s	0.90s	0.95s	1.30s	1.33s	1.16s	1.32s	0.94s
Misc.	3.50(2-OH) br 3.82(6-OH) d(4.7) 4.02(19-OH) dd(4.5,4.5)	2.08(Ac)s	2.04(Ac)s 2.05(Ac)s 2.06(Ac)s	2.000(Ac)s 2.003(Ac)s 2.06(Ac)s 1.80(9-OH)	2.03(Ac)s 2.05(Ac)s 2.09(Ac)s	2.02(Ac)s 2.04(Ac)s 2.06(Ac)s	2.05(Ac)s 2.04(Ac)s 2.07(Ac)s	2.007(Ac)s 2.061(Ac)s 2.062(Ac)s	2.03(Ac)s 2.03(Ac)s 2.05(Ac)s 3.05(OH-14) br



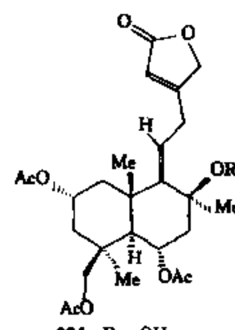
220. $R^1 = R^2 = H$

221. $R^1 = H$, $R^2 = Ac$

222. $R^1 = R^2 = Ac$

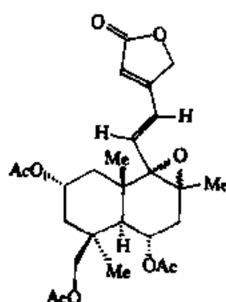


223



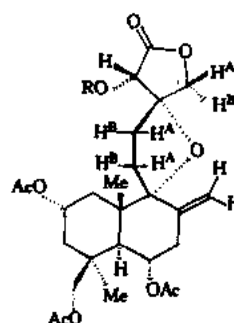
224. R = OH

225. R = H



226. 8,9-β-环氧

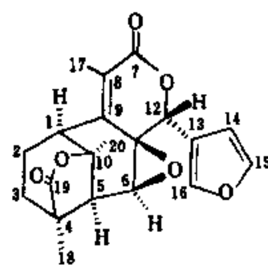
227. 8,9-α-环氧



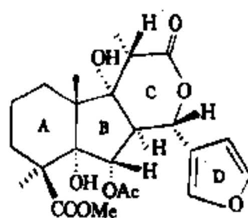
228. R = H

表 9-31 变型半日花烷衍生物 229～231 的¹H-NMR 化学位移[72]

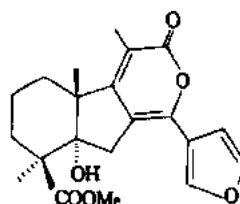
化合物 / 质子	229	230	231	化合物 / 质子	229	230	231
1-H	2.89d(6.3)	1.91brdd	—	12-H	5.10s	5.17d(11.8)	—
		(4.0,14.5)		14-H	6.22dd	6.46brdd	6.74dd
2-H	1.95m	1.75m	—		(1.0,1.9)	(1.0,1.9)	(1.1,2.2)
	1.42m	1.58m	—	15-H	7.44brt(1.6)	7.37brt(1.5)	7.46dd
3-H	1.17m	2.20td	—				(1.8,2.4)
		(4.6,13.6)		16-H	7.41m	7.50m	7.83brs
	0.91td	1.32m		17-H	2.08s	1.25d(6.6)	2.05s
	(6.2,13.8)			18-H	1.19s	0.97s	1.02s
5-H	2.58brd	—	—	20-H	1.44s	1.02s	1.34s
6-H	3.50d(2.4)	6.04d(7.9)	3.74d(15.8)	—OAc	—	1.74s	—
			2.75d(15.8)	—COOMe	—	3.67s	3.73s
8-H	—	2.88dq	—	OH	—	4.23brd(2.0)	—
		(1.9,6.4)				3.21brd(2.4)	
11-H	—	2.67dd	—				
		(7.9,11.9)					



229



230

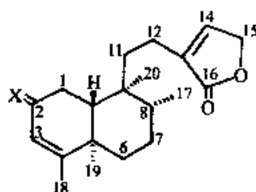


231

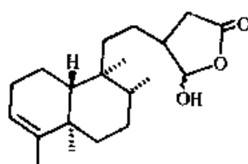
五、克罗烷衍生物的^{1}H-NMR化学位移

表 9-32 克罗烷衍生物 232～238 的^{1}H-NMR 化学位移[23,40]

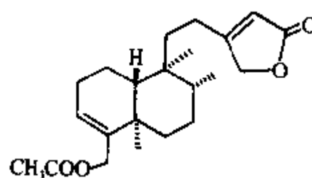
质子 \ 化合物	232	233	234	235	236	237	238
1-H	—	—	—	—	—	—	2.26m 1.91m
2-H	4.25m	5.23m	—	—	2.18m	2.35m	4.63ddd
3-H	5.23bs	5.16bs	5.74s	5.19bs	5.59bt	6.83t(3.5)	6.79d(3)
6-H	—	—	—	—	—	4.32dd(10,7)	4.25dd(10,7)
7-H	—	—	—	—	—	1.97m 1.32m	1.91m 1.34m
8-H	—	—	—	—	—	1.52m	1.91m
14-H	7.10t	7.14t	7.09t	5.84t	2.3～2.5m	5.84m	2.64dd(16,8) 2.16dd(16,8)
16-H	—	—	—	5.52bs	4.74d	4.75d(1.5)	4.40dd(9,6) 3.90dd(9,6)
17-H	0.84d	0.85d	0.88d	0.83d	0.83d	0.85d(6.5)	0.80d(6.5)
18-H	1.63bs	1.64bs	1.90d	1.60bs	4.52bs	1.26s	1.27s
19-H	1.06s	1.08s	1.13s	1.02s	1.09s	—	—
20-H	0.78s	0.77s	0.85s	0.75s	0.79s	0.77s	0.69s



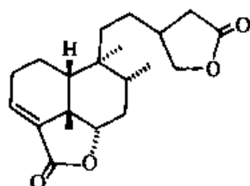
232. X = β-OH, α-H
233. X = β-OCOCH$_3$, α-H
234. X = O



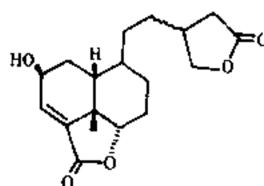
235



236



237

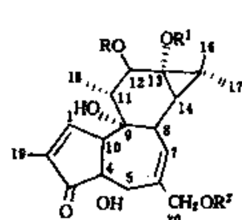


238

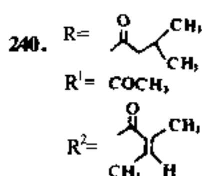
六、大戟二萜类化合物的¹H-NMR 化学位移

表 9-33　大戟二萜类化合物 239~247 的¹H-NMR 化学位移[41,42]

质子＼化合物	239	240	241	242	243	244	245	246	247
1-H	7.60m	7.61m	7.40m	7.64m	7.55m	7.60m	7.60m	7.58m	7.54bs
5-H	—	2.57	2.52	2.44	2.50	2.50	2.50	—	2.45bs
7-H	5.70d	5.71d	5.70d	5.75d	5.65d	5.62d	5.62d	5.60m	5.70d(5)
8-H	3.23	3.10	3.25	3.02	3.0	3.0	3.0	—	3.22m
10-H	3.23	3.30	3.52	3.29	3.24	3.22m	3.22m	3.24m	3.22m
12-H	—	—	5.42	1.5~2.2	—	—	—	5.48d(9.5)	5.27d(2)
14-H	—	—	—	—	—	—	—	0.94d(6)	0.98d(3)
16-H	1.28s	1.23s	1.28s	1.16s	1.20s	1.03s	1.03s	1.26s	1.22s
17-H	1.25s	1.23s	1.28s	1.16s	1.10s	1.03s	1.03s	1.21s	1.22s
18-H	—	0.97d	—	0.89d	0.86d	0.86d	0.86d	0.98d(6)	0.98d(7)
19-H	1.78m	1.80m	1.78m	1.80m	1.77m	1.76m	1.77m	1.73m	1.76d(4)
20-H	4.43	4.47	4.0	4.47	4.0	3.97	4.47	4.01s	4.43s
$OCOCH_3$	2.08s	2.08s	2.15s	2.05s	2.05s	—	2.02s	2.13s	2.05s
COR	5.3~5.45	6.08	2.8	—	—	7.31	7.31	7.28dd	—
	2.8	1.23	2.15	—	—	3.61	3.60	6.59dd	—
	2.1~2.6	1.95	2.2~2.35	—	—	—	—	6.12m	—
	1.28	1.16	1.28	—	—	—	—	5.52d	—

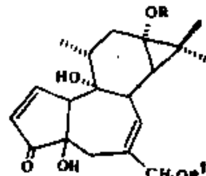


239. R = 十二烷酰基，
$R^1 = COCH_3$，
R^2 = 十七烷酰基



241. R = 十二烷酰基，
$R^1 = COCH_3$，
$R^2 = H$

247. $R = R^1 = R^2 = COCH_3$

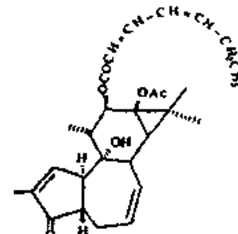


242. $R = R^1 = COCH_3$

243. $R^1 = H$，$R = COCH_3$

244. $R^1 = H$，$R = COCH_2C_6H_5$

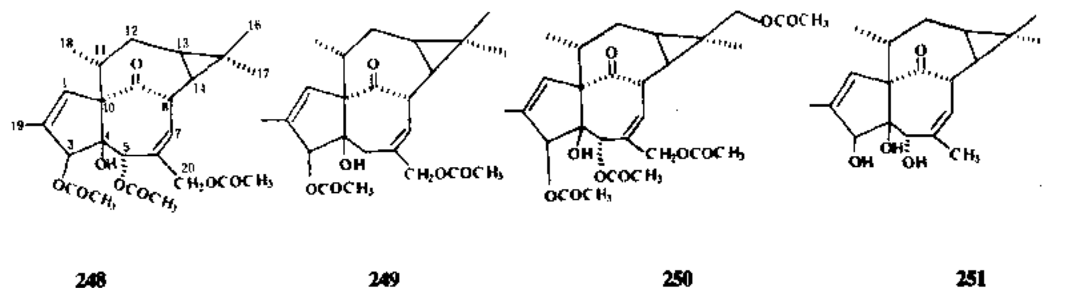
245. $R^1 = COCH_3$，$R = COCH_2C_6H_5$



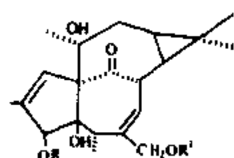
246

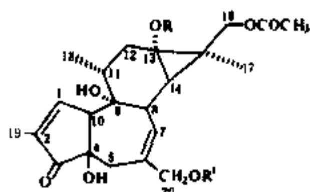
表 9-34　大戟二萜类化合物 248~257 的¹H-NMR 化学位移[41]

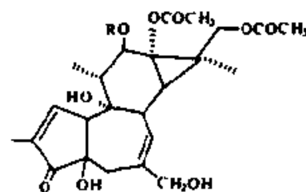
质子＼化合物	248	249	250	251	252	253	254	255	256	257
1-H	6.08s	6.09s	6.01s	6.22s	6.10m	5.94	7.57m	7.57m	7.74m	7.86m
3-H	4.97s	4.93s	5.0s	5.02s	5.6	4.45	—	—	—	—
5-H	5.38s	—	5.4s	3.86s	4.1	3.65	2.44s	2.52s	2.96m	2.91d
										3.09d
7-H	6.24d	5.82d	6.25d	5.90d	6.10m	6.1	5.66d	5.69d	6.13d	6.10d
8-H	4.25m	4.30m	4.2m	4.6m	4.1	4.1	3.07m	3.08m	4.05m	3.87m
10-H	—	—	—	—	—	—	3.27m	3.30m	3.64m	3.63m
11-H	—	—	—	—	—	—	1.97m	} 1.6~	2.90dq	2.72dq
12-H	2.02m	2.0m	2.0m	2.7m	—	—	1.5~	2.3m	6.04d	4.49d
							2.0m			
13-H	0.95m	0.92m	} 0.9~	0.6~	—	—	—	—	—	—
14-H	0.95m	0.92m	1.4m	0.9m	—	—	1.15d	1.18d	—	—
16-H	1.09s		4.22dd	1.10s	1.19	1.19	4.14q	4.15q	4.60q	4.42d
		} 1.05~								4.20d
17-H	1.12s	1.10	1.15s	1.26s	1.13	1.13	1.20s	1.20s	1.58s	1.53s
18-H	1.00d		1.00d	1.16d	—	—	0.89d	0.92d	1.63d	1.51d
19-H	1.76m	1.74m	1.77m	1.90m	1.85m	1.85m	1.76dd	1.87dd	1.69dd	1.71dd
20-H	4.58~	4.04~	4.4dd	1.98bs	4.2dd	4.65dd	4.42s	3.98s	4.36s	4.24s
	4.18dd	3.95dd								
$COCH_3$	2.22s	2.24s	2.27s	—	—	—	2.20s	—	2.10s	2.13s



248　　249　　250　　251







252. R = 十六烷酰基，R^1 = H

253. R = H，R^1 = 十六烷酰基

254. R = 当归酰基，$R^1 = COCH_3$

255. R = 当归酰基，R^1 = H

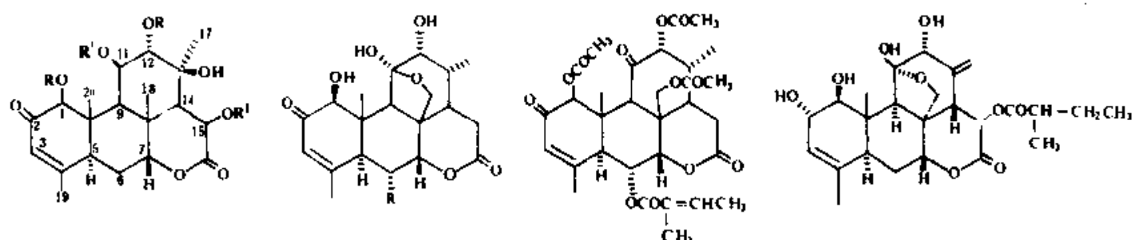
256. R = 十五烷基酰基

257. R = H

七、其他二萜类化合物的¹H-NMR化学位移

表 9-35　二萜化合物 258～264 的¹H-NMR 化学位移[43～45]

质子 \ 化合物	258	259	260	261	262	263	264
1-H	4.07s	5.32s	5.33s	4.07s	4.12s	5.20s	3.90d(5)
2-H	—	—	—	—	—	—	4.50m
3-H	6.04bs	6.02bs	6.04bs	6.13bs	6.17bs	6.03bs	5.71bs
5-H	3.05bd(13)	3.25bd(13)	3.22bd(13)	—	3.38d(11)	—	—
6-H	—	—	—	—	5.58dd	5.50dd (3,11)	—
7-H	5.28bs	4.87m	4.69m	4.47d	4.49d(2.7)	4.80d	4.69bt
9-H	2.28bs(6)	—	—	2.70s	2.77s	3.41s	3.34s
11-H	4.61m	4.38m	5.31m	—	—	—	—
12-H	4.13d(7)	4.96d(5)	5.01d(4)	3.47s	3.56d	4.77d	4.56s
14-H	—	—	—	—	—	—	3.08d(12)
15-H	4.96s	4.56d(2)	5.37d(6.4)	—	—	—	6.20d(12)
17-H	1.61s	1.73s	1.72s	1.05d	1.04d	1.03d	5.20d(12) 5.32d(2)
18-H	1.40s	1.41s	1.25s	3.60d(9) 3.90d(9)	3.74d 4.17d	4.03d(15) 4.72d(15)	3.85d(10) 4.10d(10)
19-H	1.86s	1.94s	1.97s	2.01s	2.03s	2.00s	1.56s
20-H	1.26s	1.33s	1.21s	1.18s	1.28s	1.25s	1.62s



258. R = R¹ = H
259. R = $COCH_3$, R¹ = H
260. R = R¹ = $COCH_3$

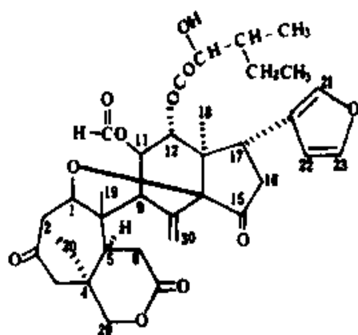
261. R = H
262. R = O—COC(CH₃)=CH—CH₃

263

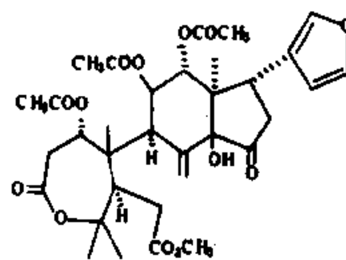
264

表 9-36 二萜化合物 265～269 的¹H-NMR 化学位移[46]

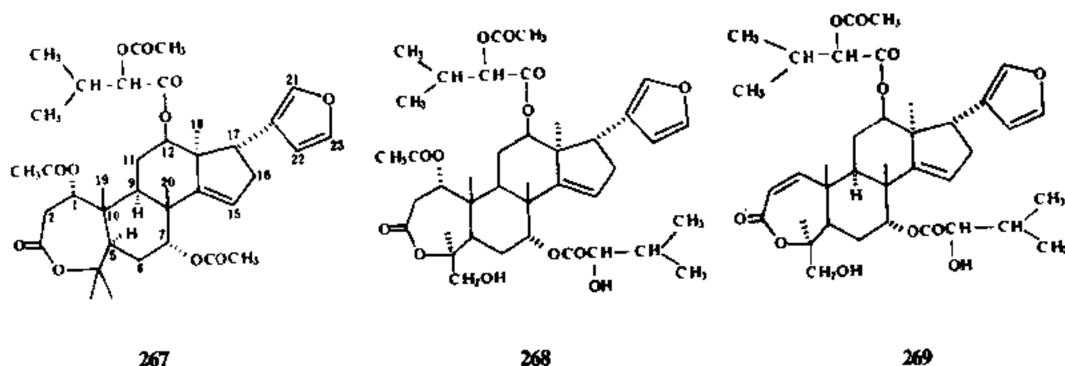
质子 \ 化合物	265	266	267	268	269
1-H	3.81m(16)	5.50m(15)	4.71m(8)	4.81m(8)	6.47d(12)
2-H	—	2.97m	3.12d(14)	3.23d(3)	5.95d(12)
7-H	—	—	5.26m(6)	5.27m(6)	5.33m
9-H	—	3.72d(7)	—	—	—
11-H	5.40m(15)	5.22m(18)	—	—	—
12-H	6.13d(12)	5.93d(11)	5.06m(17)	5.03m(18)	5.19m(16)
15-H	—	—	5.47m(5)	5.56m(6)	5.52m
16-H	—	2.41,2.89m	2.41m	2.50m	—
17-H	3.97m(20)	3.93m(20)	2.97m(17)	—	—
18-H	1.00	1.02	1.05	1.30	—
19-H	1.90	1.62	1.32	1.08	—
20-H	0.88s	1.52	1.55	1.46	—
21-H	7.22	7.21	7.15	7.15	7.23
22-H	6.22	6.23	6.21	6.21	6.28
23-H	7.36	7.32	7.31	7.31	7.35
29-H	4.14bs	—	—	4.0～4.10d(3)	4.13d,4.58d(12)
30-H	5.51s	5.75bs,6.0sbs	—	—	—
HCOO—	8.07	—	—	—	—



265



266

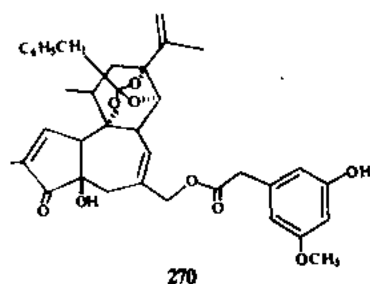


267　　268　　269

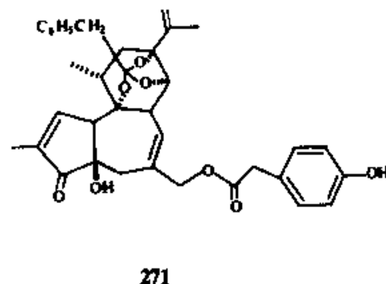
表 9-37　二萜化合物 270 ~ 274 的^{1}H-NMR 化学位移[41,47]

质子 \ 化合物	270	271	272	273	274
1-H	7.42bs	7.44bs	7.61m	1.70d(15) 2.78dd(15,9)	—
3-H	—	—	—	5.33d(8.4)	2.34m 2.84m
5-H	2.12 ~ 2.23dd	2.10 ~ 2.30dd	4.23s	5.83s	6.34t
7-H	5.84d	5.88d	3.46s	5.09d(1.4)	—
8-H	3.05m	3.05m	2.94d	—	5.89d
9-H	—	—	—	1.24 ~ 1.32dd	6.04d
10-H	3.05m	3.06m	3.84m	—	—
11-H	2.60m	2.56m	—	1.24 ~ 1.32d	—
12-H	2.10m	2.15m	—	4.86dd(11,3.6)	—
13-H	—	—	—	2.93q(3.7)	5.37
14-H	4.18d	4.18d	4.45d	—	4.88
16-H	4.70s	4.72s	4.90 ~ 5.04dd	0.97d(7)	—
17-H	1.52s	1.52bs	1.80s	2.10bs	0.95s
18-H	0.96d	0.96d	1.18d	0.85*①s	1.77s
19-H	1.81dd	1.81dd	1.80bs	1.12*s	2.08bs
20-H	4.53s	4.56s	3.84s	1.06d(7)	1.17s

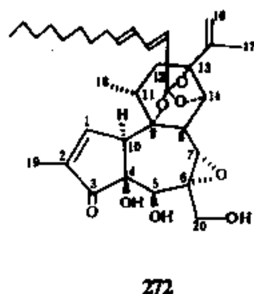
① “*”表示两个数字可以互相交换。



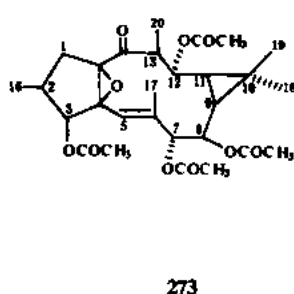
270



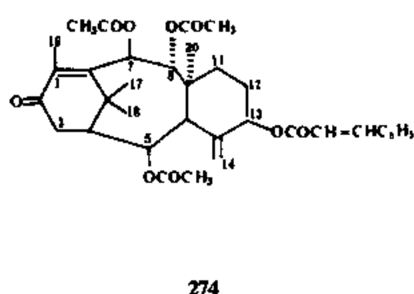
271



272



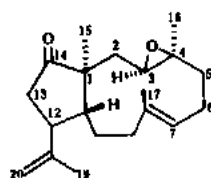
273



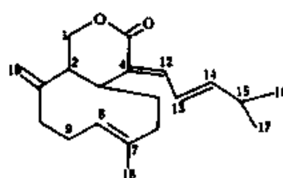
274

表 9-38 二萜化合物 275～281 的 ^{1}H-NMR 化学位移[48～51]

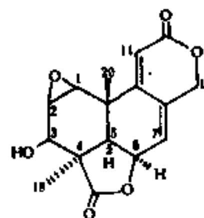
质子 \ 化合物	275	276	277	278	279	280	281
1-H	—	—	—	3.54dd (12,12) 4.05dd (12,6)	3.61dd (11,11) 4.08dd (11,6)	3.63d(4.4)	5.63d(6)
2-H	1.93dd (15,3)	—	1.79dd (14,3)	—	—	3.38dd (4.4,6.1)	—
3-H	2.99dd (11,3)	2.94dd (11,3)	2.91dd (11,3)	—	—	4.30d (6.1)	7.45s
5-H	—	—	—	—	—	2.22d (5.6)	4.06ddd (9,2,2)
6-H	—	—	—	—	—	5.09dd (5.6,4.4)	5.61dd (6,2)
7-H	5.10bd(12)	5.01bd(11)	5.04bd(10)	—	—	6.36 (4.4,1.5)	6.02dd (6,2)
8-H	—	—	—	5.38m	5.32d(8)	—	—
9-H	—	—	—	—	—	—	3.35dd (9,6)
10-H	—	—	—	—	—	—	5.21bs
11-H	—	—	—	—	—	6.22d(1.5)	—
12-H	2.87ddd (14,7,7)	2.34	2.79ddd (11,7,7)	6.86d(12)	6.92d(11)	—	—
13-H	—	—	—	6.4～6.04m	6.53dd (15,11)	—	7.55bs
14-H	—	3.62dd (9,5)	4.86dd(7.3)	6.04～6.4m	6.26d(15)	5.04dd	6.97d(2.5)
15-H	1.24s	1.21s	1.24s	—	—	—	—
16-H	1.33s	1.21s	1.32bs	1.04d	1.38s	—	—
17-H	1.66bs	1.56bs	1.57bs	1.04d	1.38s	—	6.80d
18-H	—	—	—	1.69d(1)	1.70bs	1.10s	6.89dd
19-H	1.77bs	1.69bs	1.72bs	4.94s, 4.82s	5.09s, 4.91s	—	—
20-H	4.73bs, 5.02bs	4.66bs, 4.89bs	4.65bs, 4.90bs	—	—	1.38s	—



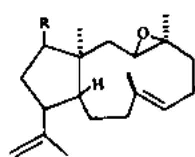
275



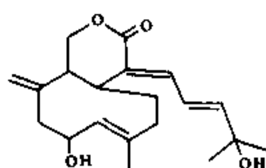
278



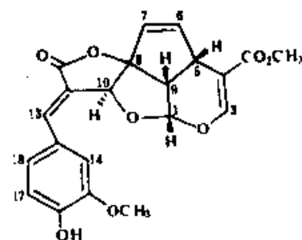
280



276. R = OH
277. R = OCOCH$_3$



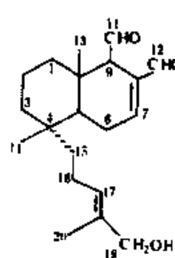
279



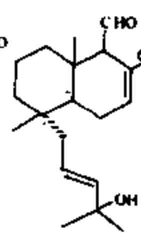
281

表 9-39　二萜化合物 282～288 的^{1}H-NMR 化学位移[52]

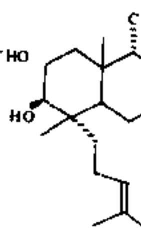
质子＼化合物	282	283	284	285	286	287	288
3-H	—	—	3.50t(7)	3.45t(7)	—	—	—
7-H	7.03m	7.03m	6.93m	6.70m	5.70bs	5.81m	5.85m
9-H	—	—	3.60bs	—	—	—	—
11-H	9.50d(5)	9.50d(5)	9.70d(2)	4.30m	3.77～4.40m	4.20m	4.20m
12-H	9.38s	9.37s	9.30s	—	—	4.50bs	4.50bd
13-H	1.00s	1.00s	0.96s	—	0.83s	0.87s	0.90s
14-H	0.93s	0.93s	0.93s	0.87s	0.77s	0.72s	0.83s
16-H	—	5.53m	—	—	—	—	5.56m
17-H	5.30t(7)	5.53m	5.00t(7)	5.30t(7)	5.53t(7)	5.02t(7)	5.56m
19-H	3.42bs	1.33s	1.58bs	1.53bs	3.40bs	4.85bs	1.30s
20-H	1.70s	1.33s	1.63bs	1.63bs	1.68bs	1.67	1.30s



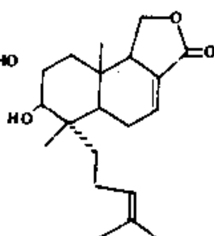
282



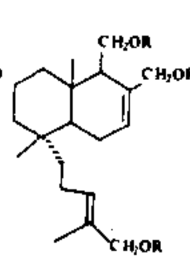
283



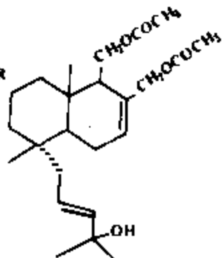
284



285



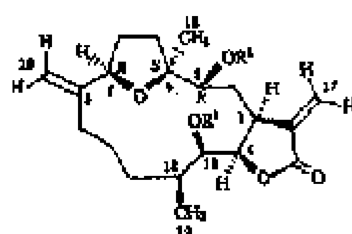
286. R = H
287. R = COCH$_3$



288

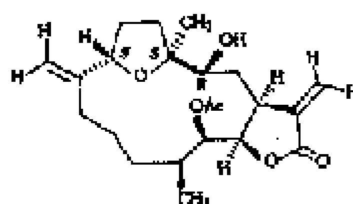
表 9-40 二萜化合物 289～293 的 ^{1}H-NMR 化学位移[75]

质子 \ 化合物	289	290	291	292	293
1-H	3.43(1H)brm	3.45,1H,m	3.41,1H,m	3.16,1H,m	3.14,1H,m
2α-H	1.95,1H,m	1.93,1H,m	2.20,1H,m	2.10,1H,m	2.12,1H,m
2β-H	1.48,1H,m	1.32,1H,m	1.78,1H,m	1.91,1H,m	1.80,1H,m
3-H	3.43,1H,br m	3.36,1H,m	3.88,1H,dd(3.6,8.4)	3.54,1H,dd(3.1,10.6)	3.26,1H,m
5α-H	1.82,1H,m	1.76,1H,m	1.97,1H,m	1.72,1H,m	1.49,1H,m
5β-H	1.73,1H,m	1.76,1H,m	1.80,1H,m	2.77,1H,dt	2.16,1H,m
6α-H	1.92,1H,m	1.95,1H,m	1.98,1H,m	1.77,1H,m	1.82,1H,m
6β-H	1.92,1H,m	1.78,1H,m	1.77,1H,m	1.47,1H,m	1.49,1H,m
7-H	4.49,1H,dd(6.4,8.5)	4.48,1H,m	4.39,1H,br d(10.2)	3.35,1H,br d(12.0)	3.28,1H,m
9α-H	2.49,1H,br(11.1)	2.53,1H,m	2.01,1H,m	1.88,1H,m	1.95,1H,m
9β-H	1.71,1H,m	1.63,1H,m	1.78,1H,m	1.33,1H,m	1.47,1H,m
10α-H	1.62,1H,m	1.62,1H,m	1.48,1H,m	1.81,1H,m	1.70,1H,m
10β-H	1.62,1H,m	1.62,1H,m	1.48,1H,m	1.75,1H,m	1.48,1H,m
11α-H	1.44,1H,m	1.80,1H,m	2.22,1H,m	2.40,1H,m	2.40,1H,m
11β-H	1.18,1H,m	1.18,1H,m	1.81,1H,m	1.32,1H,m	1.44,1H,m
12-H	1.87,1H,m	1.82,1H,m	2.19,1H,m	2.10,1H,m	2.14,1H,m
13-H	5.41,1H,brd(9.6)	3.96,1H,d(9.6)	5.48,1H,dd(4.8,7.2)	5.36,1H,d(10.8)	5.39,1H,d(10.8)
14-H	4.60,1H,dd(6.0,9.3)	4.48,1H,m	4.74,1H,t(6.9)	5.54,1H,d(8.1)	5.47,1H,d(8.1)
17α-H	6.24,1H,br s	6.26,1H,br s	6.18,1H,d(1.8)	6.11,1H,d(3.6)	6.10,1H,d(3.6)
17β-H	5.70,1H,br s	5.74,1H,br s	5.58,1H,d(1.8)	5.32,1H,d(3.6)	5.35,1H,d(3.0)
18-Me	1.35,3H,s	1.38,3H,s	1.17,3H,s	1.14,3H,s	1.15,3H,s
19α-H	5.03,1H,brs	5.03,1H,brs	4.92,1H,brs	1.64,3H,s	1.32,3H,s
19β-H	4.95,1H,brs	4.97,1H,brs	4.87,1H,brs	—	—
20-Me	0.96,3H,d(6.9)	0.96,3H,d(6.0)	0.93,3H,d(6.9)	0.78,3H,d(6.9)	0.79,3H,d(6.9)
22-Me	2.08,3H,s	-	2.04,3H,s	1.87,3H,s	1.87,3H,s
23-Me	—	—	—	-	3.24,3H,s
24-Me	—	—	—	1.99,3H,s	—

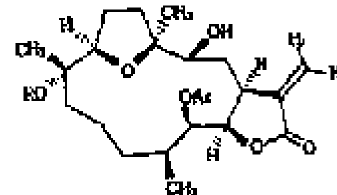


289. R^1 = Ac, R^2 = H

290. R^1 = R^2 = H



291

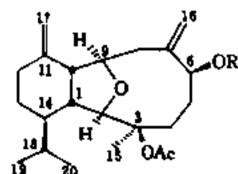


292. R = Ac

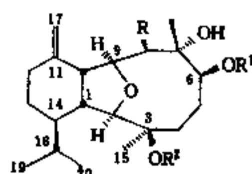
293. R = CH_3

表9-41 二萜化合物294～302的^{1}H-NMR化学位移[illegible]

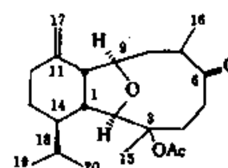
化合物 / 质子	294	295	296	297	298	299	300	301	302
1-H	[illegible]	2.20m	2.25m	2.20m	2.26m	2.18m	2.21m	2.25m	2.18m
2-H	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]



296. R = H



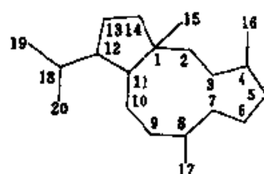
294. R = H, R^1 = $COCH_2CHMe_2$, R^2 = Ac
295. R = R^1 = H, R^2 = $COCH_2CH_2CH_3$
299. R = OH, R^1 = H, R^2 = Ac
300. R = R^1 = H, R^2 = Ac
301. R = OH, R^1 = Et, R^2 = Ac
302. R = H, R^1 = Et, R^2 = Ac

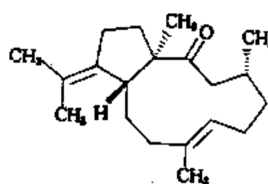


297, 298. 立体异构体

表 9-42　二萜化合物 303～307 的 ^{1}H-NMR 化学位移[75]

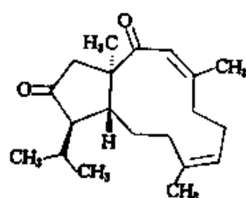
质子＼化合物	303	304	305	306	307
1-H	—	—	—	—	—
2′-H	—	—	—	2.46dd(10.5,13.2)	2.15m
2″-H	—	—	—	1.84m	1.74m
3′-H	2.49dd(10.2,18.9)	6.30brs	6.35brs	5.08dd(5.1,10.8)	4.99dd(3.0,10.8)
3″-H	2.22dd(3.0,18.9)	—	—	—	—
4-H	2.13m	—	—	—	—
5′-H	1.93m	3.09m	3.20dd(5.7,12.9)	2.20m	2.09m
5″-H	1.41m	1.93m	1.99m	2.10m	2.07m
6′-H	1.98m	2.65m	2.74m	2.27m	2.16m
6″-H	1.89m	1.79m	1.82m	2.12m	2.12m
7-H	4.95m	5.02brd(12.0)	4.99brd(10.8)	4.89m	4.91brt,6.5
8-H	—	—	—	—	—
9′-H	2.03brt(6.3)	2.17m	1.84m	2.05m	1.96m
9″-H	2.03brt(6.3)	1.63m	1.50m	1.54m	1.44m
10′-H	1.61m	1.98m	2.34m	1.25m	1.66m
10″-H	1.61m	1.32m	1.67m	1.25m	1.28m
11-H	2.73brm	2.99brd(12.0)	2.35m	1.77m	1.66m
12-H	—	—	1.80m	—	—
13′-H	2.35dd(7.2,14.4)	2.44dd(7.0,14.7)	—	2.07m	1.95m
13″-H	2.13m	2.32m	—	1.88m	1.73m
14′-H	1.78dd(5.5,12.5)	1.89m	2.64d(17.7)	1.83m	1.74m
14″-H	1.41m	1.45m	2.11dd(1.8,17.7)	1.46dd(4.2,8.4)	1.51m
15-H	1.15s	1.14s	1.08s	0.98s	1.01s
16-H	0.94d(6.9)	1.80s	1.83s	1.57s	1.52s
17-H	1.61s	1.69s	1.62s	1.59s	1.54s
18-H	—	—	1.97m	—	—
19-H	1.61s	1.67s	1.11d(6.9)	1.83s	1.81s
20′-H	1.61s	1.61s	0.98d(6.9)	5.01brs	5.12brs
20″-H	—	—	—	4.93brs	4.84brs



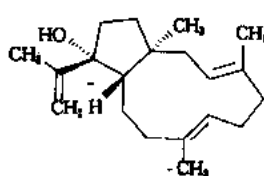


303

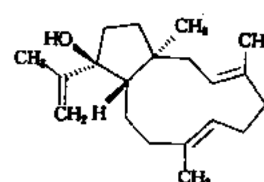
304



305



306



307

表 9-43 二萜化合物 308 - 315 的 ^{1}H-NMR 化学位移[36]

质子 \ 化合物	308	309	310	311	312	313	314	315
2-H	1.37m	4.99d(9.6)	5.19d(10.8)	2.25m, 1.86m	2.06m, 1.87m	1.94m	1.35m, 1.51m	3.19br dd(12.8, 12.9), 1.80dd (4.2, 12.9)
3-H	2.19ddd(1.2, 4.1, 8.8)	2.35dd(1.1, 9.8)	3.09br d(10.8)	5.40br d(12.2)	5.24br d(11.4)	5.29m	2.41dd(3.6, 11.2)	6.03dd(4.2, 12.8)
5-H	5.58br m	5.01br m	5.78m	2.27m	2.38br dd(6.8, 16.6), 2.71br dd (7.3, 16.6)	2.73ddd(2.2, 5.8, 14.5), 2.40m	5.60br d(5.7)	2.17m, 2.79m
6-H	5.86dd(5.0, 9.5)	5.99br d(9.4)	5.84dd(5.4, 9.7)	1.99m, 1.60m	5.84dddd(1.5, 6.6, 7.3, 10.6)	5.77dddd(1.0, 5.8, 8.4, 10.6)	5.80dd(5.7, 9.8)	2.05m, 2.31m
7-H	5.94br d(9.5)	5.99dd(4.7, 9.4)	6.00d(9.7)	2.65dd(2.1, 10.9)	5.52ddd(1.8, 8.0, 10.6)	5.54ddd(2.2, 8.5, 10.6)	5.96d(9.8)	5.23br d(11.2)
8-H					3.35m	3.47br dq(7.3, 7.3)		
9-H				3.40br d(4.5)				5.40dd(6.5, 10.5)
10-H	2.31dd(2.1, 12.5), 2.66dd(11.9, 12.5)	2.36dd(3.0, 13.5), 2.72dd(12.1, 13.5)	2.90dd(7.8, 15.8), 2.89dd(11.9, 15.8)	2.41m, 1.63m	2.57dd(6.5, 16.1), 2.24dd(4.6, 16.1)	2.66dd(7.5, 16.7), 2.25br d(16.7)	2.62d(10.1), 2.30d (9.3)	2.00m, 1.67m
11-H	1.45dd(2.1, 11.9)	1.80m	2.27dd(7.8, 11.9)	1.83dd(8.5, 2.0)	2.02m	2.04dd(1.8, 7.5)	2.26dd(9.3, 10.1)	2.00m
13-H	1.40m, 1.55m	1.49m, 1.60m	2.00m, 1.57m	1.32m, 1.58m	1.29m, 1.67m	1.30m, 1.60m	1.30m, 1.50m	5.19br s
14-H	1.60m, 1.10m	1.45m, 1.30m	1.75m, 1.34m	1.42m, 1.90m	1.53m, 1.67m	1.58m, 1.94m	1.97m, 1.60m	2.00m, 2.32m
15-H	1.17br m	1.18m	0.99m	1.65m	1.06m	1.16m	0.96m	1.28m
16-H	1.78s	1.86br s	1.81s	1.65br s	1.62br s	1.44br s	1.78m	
17-H	1.12s	1.14s	1.36s	1.30s	1.16d(7.1)	1.21d(7.3)	1.17s	1.54br s
18-H	1.75m	1.76m	1.66m	2.15m	1.63m	1.70m	1.67m	2.15m
19-H	0.83d(6.7)	0.88d(6.7)	0.93d(6.5)	0.93d(6.9)	0.90d(6.8)	0.95d(6.8)	0.96d(6.7)	0.89d(6.6)
20-H	0.96d(6.7)	0.98d(6.7)	0.95d(6.5)	0.98d(6.9)	0.92d(6.8)	0.98d(6.8)	0.97d(6.7)	1.06d(6.6)
OAc		2.00s						2.00s

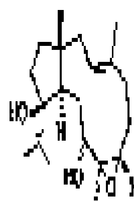


308. R = H

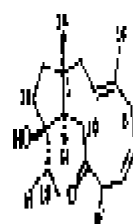
309. R = OAc



310

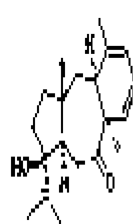


311

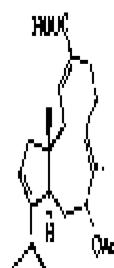


312. R = β-CH_3

313. R = α-CH_3



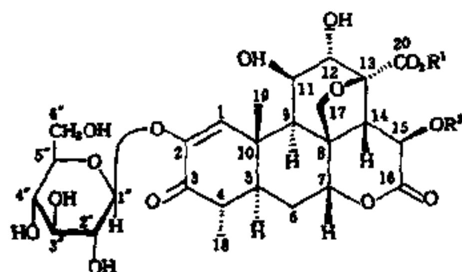
314



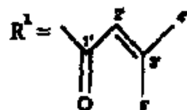
315

表 9-44 二萜化合物 316～321 的 ^{1}H-NMR 化学位移[77]

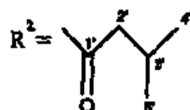
质子 \ 化合物	316	317	318	319	320	321
1-H	7.31s	7.29s	7.31s	7.28s	7.27s	7.31s
4-H	2.42dq	2.40dq	2.42dq	2.40m	2.40m	2.43m
5-H				3.35		
6α-H	2.04br d	2.02br d	2.04br d	2.02	2.00	2.03
6β-H	1.68br d	1.67br d	1.69br d	1.64	1.64	1.65
7-H	4.99br s	4.96br s	5.00br s	5.00	4.97	5.10
9-H	2.55d(5.0)	2.52d(4.5)	2.56d(5.0)	2.52d	2.50d	2.54d
11-H	5.23d(5.0)	5.21d(4.5)	5.23br d	5.21	5.20	5.21
12-H	5.20br d	5.14br d	5.23br d	5.13	5.13	5.18
14-H						
15-H				6.90br d	6.92br d	6.90br d
17α-H	3.95m	3.94m	3.95d(7.0)			
17β-H	5.12d(7.5)	5.10d(7.5)	5.11m			
4-Me	1.18d(6.5)	1.16d(6.5)	1.18d(7.0)	1.18d	1.15d	1.17d
10-Me	1.64s	1.63s	1.64s	1.64s	1.60s	1.62s
20-OMe	—	—	—	3.78s	3.82s	3.88s
2′-H	5.79m	2.32d(7.5)	6.13s	5.85s		6.09s
3′-H	—	2.21dq	—	—	2.22m	—
3′-Me	1.45s	0.84d(6.5)	2.25s	1.68s	0.95d	2.25s
	2.09s	0.87d(6.5)	—	2.17s	0.97d	—
4′-Me	—	—	1.27s	—	—	1.40s
	—	—	1.27s	—	—	1.44s
4′-OAc	—	—	1.86s	—	—	1.93s
1″-H	5.39d(7.0)	5.36d(7.5)	5.38d(7.0)	5.38d	5.36d	5.39d
2″-H	4.28m	4.28m	4.28m			
3″-H	4.27m	4.27m	4.26m			
4″-H	4.26m	4.25m	4.25m			
5″-H	3.94m	3.92m	3.94m			
6″-H	4.23m	4.22m	4.23m			
	4.49dd (12.3)	4.49dd (12.3)	4.49dd			



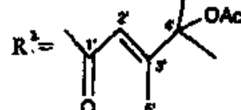
316. R^1 = H,



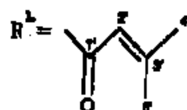
317. R^1 = H,



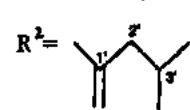
318. R^1 = H,



319. R^1 = Me,



320. R^1 = Me,



321. R^1 = Me,

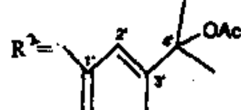
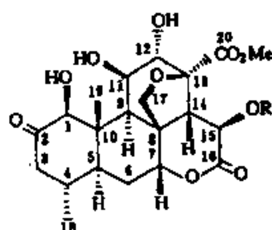
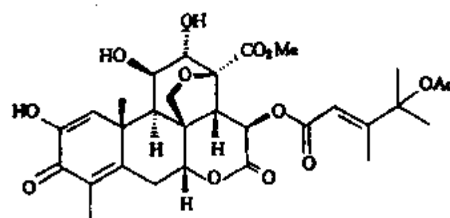
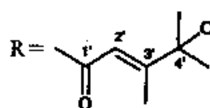


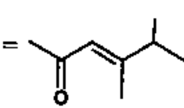
表 9-45　二萜化合物 322～326 的^{1}H-NMR 化学位移[78]

质子 \ 化合物	322	323	324	325	326
1-H	—	—	7.10s	—	—
1α-H	4.26brs	2.23brs	—	—	—
2-H	—	—	—	5.07dd(12.0,4.4)	—
3-H	—	—	—	—	5.87s
3α-H	2.21dd(13.8,12.6)	2.21dd(13,13)	—	2.93dd(13.2,12.0)	—
3β-H	2.50dd(13.8,4.6)	2.49d(13)	—	2.24dd(13.2,4.4)	—
4-H	1.70m	1.68m	—	1.73m	2.30m
5-H	2.01brs	1.96brd(2)	—	2.55dd(12.8,2.0)	2.17
6α-H	2.16dd(12.6,2)	2.13dd(12,2)	3.35dd	2.17dd(12.8,2.0)	2.20dd(13,13)
6β-H	1.53dd(13,12.6)	1.52ddd(12,12,2)	2.82d	1.48ddd(12.8,12.8,2.0)	1.63dd(13,13)
7-H	5.00brs	4.99dd(2,2)	5.31d	4.91brs	4.95
9-H	2.72d(3.8)	2.70d(4)	2.60d	3.53brs	2.99
11-H	5.34brs	5.34d(4)	—	5.03d(4.0)	6.52d(5)
12-H	5.15brs	5.14brd	—	4.62d(4.0)	5.16
14-H	4.04brs	4.01brd	4.13brd	4.04brs	4.04brd
15-H	6.70brs	4.68brd	—	6.39d(4.8)	4.90brd
17α-H	3.88d(8.0)	3.87d(7)	4.07d	3.93d(6.8)	3.92d(7.5)
17β-H	4.99d(8.0)	4.98d(7)	5.32d	5.09d(6.8)	5.17d(7.5)
2'-H	6.10s	5.88s	6.03s	5.83s	5.87s
4'-H	—	2.14m	—	1.80m	2.14m
4-Me	0.85d(6.5)	0.84d(6)	2.23s	0.81d(6.4)	0.98d(7)
10-Me	1.36s	1.35s	1.92s	1.54s	1.91s
3'-Me	2.26s	2.17s	2.24d	2.11s	2.17s
4'-Me	1.39s	0.85d(7.5)	1.33s	0.78d(6.4)	0.85d(7)
	1.44s	0.85d(7.5)	1.41s	0.78d(6.4)	—
4'-OAc	1.94s	—	1.94s	—	—
20-OMe	3.86s	3.75s	3.90s	3.75s	3.76s

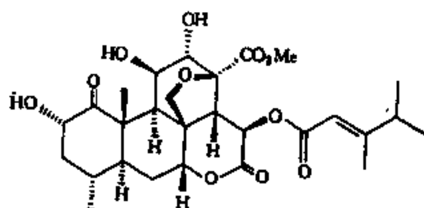




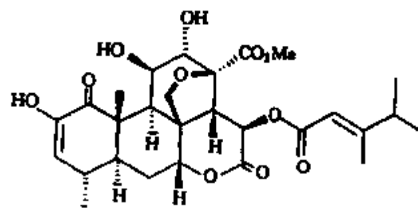
322.


323.


324

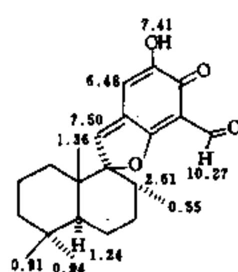


325

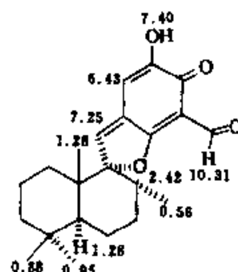


326

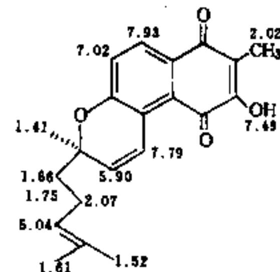
其他二萜化合物 327 ~ 340 的^{1}H-NMR 化学位移如下：



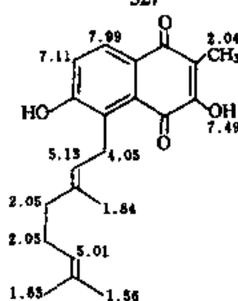
327[79]



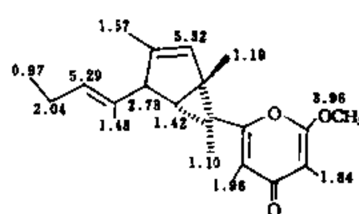
328[79]



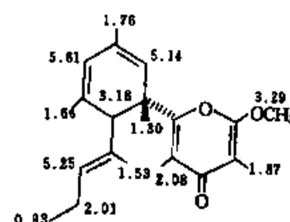
329[80]



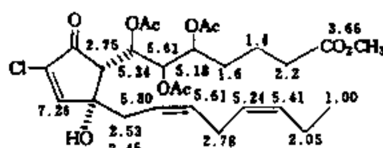
330[80]



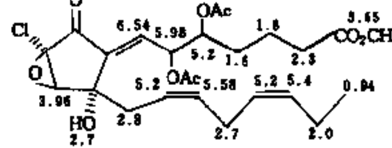
331[81]



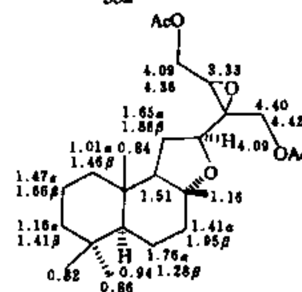
332[81]



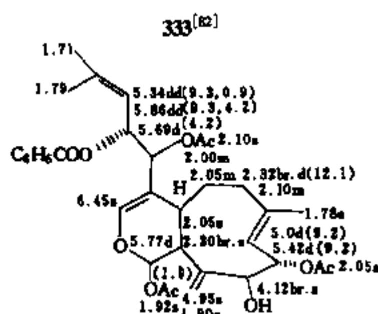
333[82]



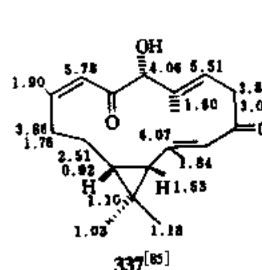
334[82]



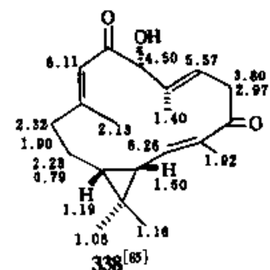
335[83]



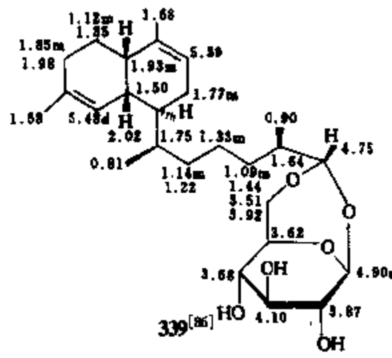
336[84]



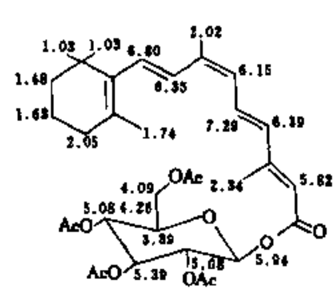
337[85]



338[85]



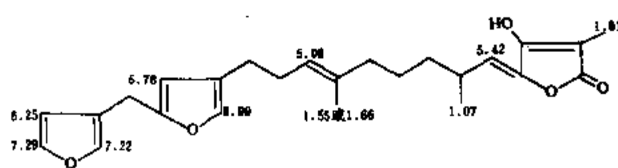
339[86]



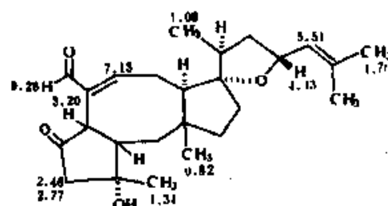
340[87]

第二节 二倍半萜叠烯衍生物及三萜类化合物的^{1}H-NMR 化学位移

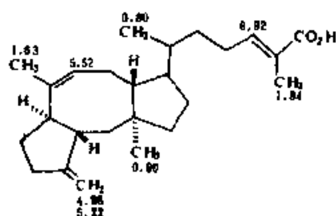
一、二倍半萜及叠烯衍生物的^{1}H-NMR 化学位移[53~56]



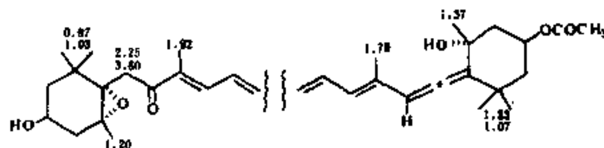
341



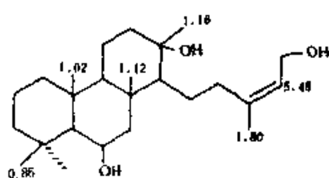
342



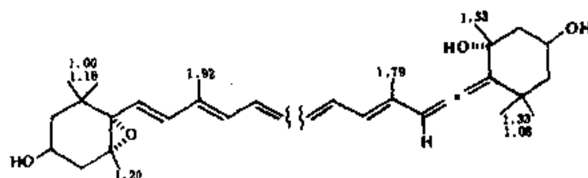
343



344



345

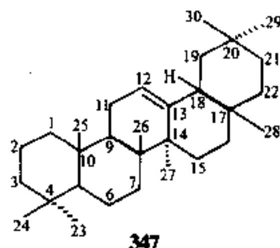


346

二、齐墩果烷衍生物的^{1}H-NMR 化学位移

表 9-46 齐墩果烷(347)衍生物甲基化学位移的基本值[57]

取代基＼质子	23-H	24-H	25-H	26-H	27-H	28-H	29-H	30-H
无取代	0.88	0.84	0.94	0.98	1.15	0.84	0.88	0.88
3β-OH	0.99	0.79~0.80	0.94~0.95	0.97~1.01	1.13~1.15	0.83~0.85	0.87~0.88	0.87~0.88
3β-OCOCH$_3$	0.86~0.88	0.86~0.88	0.96~0.98	0.96~0.98	1.13~1.14	0.83~0.84	0.86~0.88	0.86~0.88
3β-OCOC$_6$H$_5$	0.96	1.01~1.03	1.01~1.03	1.00	1.16	0.85	0.88	0.88
3-酮	1.10	1.03	1.07	1.08	1.15	0.85	0.88	0.88
28-CO$_2$H	0.87	0.82	0.91~0.94	0.76	1.15	—	0.91~0.94	0.91~0.94
28-CO$_2$CH$_3$	0.87	0.82	0.91~0.93	0.73	1.14	—	0.91~0.94	0.91~0.94



347

表 9-47 取代基对齐墩果烷(347)衍生物甲基化学位移的影响[57]

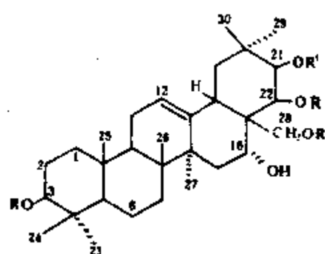
基本结构	第二取代基	化学位移变化							
		23-H	24-H	25-H	26-H	27-H	28-H	29-H	30-H
3β-OH	2α-OH	0.03	0.03	0.03	-0.01	-0.01	—	-0.02	-0.02
	2α-$OCOCH_3$	0.03	0.08	0.13	-0.03	-0.03	—	-0.02	-0.02
	2β-OH	—	0.22	0.32	0.02	0	—	0.01	0.01
	6α-OH	0.31	0.19	0.03	0.03	0.01	—	-0.01	-0.01
	7β-OH	0	0.01	0	0.05	0.11	—	—	—
	16α-OH	0	0	-0.03	-0.03	0.17	—	0.05	0.05
	16β-OH	0	0	-0.01	0.05	0.03	—	0.03	0.03
	19α-OH	-0.01	0	-0.01	0	0.11	—	0.04	0.04
	19β-OH	—	0.01	0.02	0.03	0.03	—	0.01	0.01
	21β-OH	-0.01	0	-0.01	-0.01	-0.01	—	0.05	-0.01
	22α-OH	-0.01	0	-0.01	0.01	0.02	0.15	0.06	0.06
	22β-OH	0	0	0.02	0.02	-0.01	0.08 或 0.05	0.01 或 0.04	0.17
	23-OH	—	0.08	0.01	-0.03	-0.01	—	-0.04	-0.03
	28-OH	0.01	0	0.01	-0.02	0.05	—	0	0
	28-CO_2CH_3	-0.01	-0.01	-0.02	-0.26	0	—	0.04	0.05
	29-OH	0	-0.01	0	0.01	0	—	—	0.03
3β-$OCOCH_3$	2α-$OCOCH_3$	0.04	0.04	0.13	-0.01	-0.01	—	-0.02	-0.02
	2β-$OCOCH_3$	—	0.18	0.26	0.03	0	—	0	0
	6α-$OCOCH_3$	0.08	0.21	0.12	0.12	0.03	—	0.01	0.01
	7β-$OCOCH_3$	0.01	0.03	0.04	0.13	0.08	-0.04	0.27	—
	16α-$OCOCH_3$	-0.01	-0.01	0.01	-0.04	0.11	—	0.05	0.05
	16β-$OCOCH_3$	-0.01	-0.01	0	0.05	0.10	—	0.03	0.03
		—	0.01	0.03	0.01	0.13	—	0.08,0.02	—
	21β-$OCOCH_3$	0	0	0	-0.01	-0.01	—	-0.07	0.05
	22α-$OCOCH_3$	0.01	0.01	0.01	0.01	0.04	0.04	0.06	0.11
	22β-$OCOCH_3$	0.01	0.01	0.02	0.02	0.02	0.15 或 -0.01	-0.04 或 0.12	0.01
	23-$OCOCH_3$	—	-0.03	0.03	0	-0.02	—	0.02	0.02
		—	-0.03	0.03	0.01	-0.03	—	-0.02	-0.02

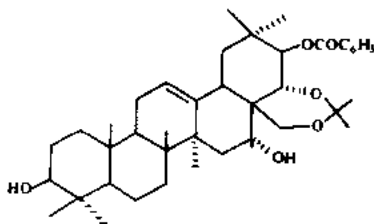
续表

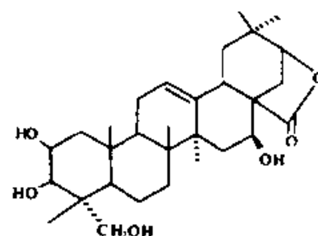
基本结构	第二取代基	化学位移变化							
		23-H	24-H	25-H	26-H	27-H	28-H	29-H	30-H
3β-OCOCH$_3$	24-OCOCH$_3$	0.16	—	-0.01	-0.01	-0.01	—	-0.01	0
		0.12	—	0.05	-0.01	-0.01	—	0	0
	28-OCOCH$_3$	0.01	0.01	0	0	0.04	—	0.01	0.01
	29-OCOCH$_3$	0	0	0.02	-0.01	-0.01	—	—	0.07
	30-OCOCH$_3$	0	0	0	0.01	0	—	0.04	—
	19-酮	0	0	0.03	0.02	-0.14	—	0.16或0.26	0.16或0.26
3-酮	28-CO$_2$CH$_3$	0	0.01~0.03	-0.03~0	-0.28	0.01	—	0.03	0.03
	28-CO$_2$H	-0.01	0~0.03	-0.03~-0.01	-0.27	0	—	0.03~0.06	0.03~0.06
	28-CH$_2$OH	-0.01	-0.03	-0.01	-0.02	0.03	—	0	0
	29-CO$_2$CH$_3$	0	0	0	-0.02	0	0.02	—	0.32
28-CO$_2$H	3β-OCOCH$_3$	0	0.05	-0.03~0.04	0	0	—	-0.03~0.04	-0.03~0.04
	3-酮	0.06	0.22~0.24	0.09~0.15	0.06	0	—	-0.03~0.03	-0.03~0.03
28-CO$_2$CH$_3$	3β-OH	0.13	-0.03	-0.02~0.04	0.01	0.01	—	-0.03~0.04	-0.03~0.04
	3β-OCOCH$_3$	0	0.05	-0.02~0.05	0.01	0	—	-0.03~0.05	-0.03~0.05
	3-酮	0.23	0.23~0.25	0.11~0.16	0.04	0.01	—	-0.03~0.01	-0.03~0.01

表 9-48 齐墩果烷衍生物 348~354 的^{1}H-NMR 化学位移[58~61]

质子 \ 化合物	348	349	350	351	352	353	354
2-H	—	—	—	—	4.00q(4.8,12)	—	4.43m
3-H	—	—	—	—	3.62d(3.6)	3.66m	4.12d(4)
12-H	5.44m	5.54bs	5.42m	5.31bs	5.40t	5.33m	5.46bs
16-H	4.28m	4.68bs	4.72m	4.84bs	4.11t(3.7)	3.66m	—
21-H	5.56d	6.16d(10)	5.60d(10)	3.98d(11)	4.24d(5.4)	5.00d	—
22-H	5.64d	6.28d(10)	5.84d(10)	5.82d(11)	—	—	—
23-H	—	—	—	—	3.42d(10)	—	3.70d(10)
					3.71d(10)		4.08d(10)
28-H	3.74bs	4.14d(12)	3.74bs	3.48dd	—	—	—
		4.28d(12)					
CH$_3$	—	—	—	—	1.05s	0.66s	1.22s
	—	—	—	—	1.24s	0.70s	1.51s
	—	—	—	—	1.03s	1.0s	0.92s
	—	—	—	—	1.22s	1.33s	1.25s
	—	—	—	—	1.02s	—	1.01s
	—	—	—	—	1.02s	—	0.99s







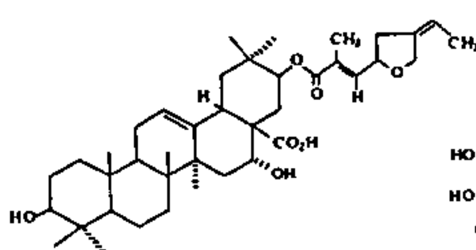
348. $R^1 = R = COCH_3$

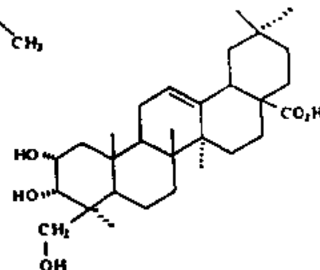
349. $R^1 = R = COC_6H_5$

350. $R^1 = COC_6H_5$, $R = COCH_3$

351

352



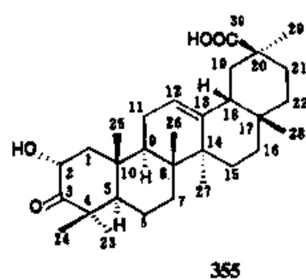


353

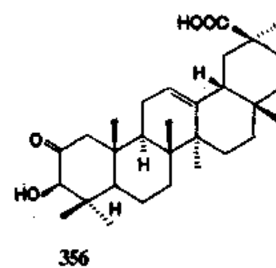
354

表 9-49 齐墩果烷衍生物 355~358 的 ^{1}H-NMR 化学位移[88]

质子 \ 化合物	355	356	357	358
1α-H	2.42	2.07d(12.2)	—	—
1β-H	1.12dd(6.7,12.6)	2.49d(12.2)	3.97dd(3.0,3.6)	—
1-H	—	—	—	7.05d(10.1)
2α-H	—	—	2.37dd(3.0,16.2)	—
2β-H	4.56dd(6.5,12.6)	—	3.06dd(3.6,16.2)	—
2-H	—	—	—	5.81d(10.1)
3α-H	—	3.91s	—	—
5-H	1.21	1.48	1.75	1.58
6-H	1.55	1.48,1.70	1.57	1.58
7-H	1.39,1.55	1.42,1.64	1.40,1.60	1.45,1.60
9-H	1.63	1.89	2.42	1.88
11-H	1.97	1.88	1.96	2.12
12-H	5.31brt	5.30brt	5.31brt	5.37brt
15-H	1.01,1.79	1.04,1.81	1.01,1.83	1.02,1.84
16-H	0.92,1.93	0.92,1.96	0.91,1.93	0.92,1.96
18-H	1.99	2.01	2.00	2.03
19-H	1.60,1.86	1.63,1.86	1.62,1.88	1.67,1.88
21-H	1.37,1.93	1.38,1.97	1.35,1.92	1.39,1.96
22-H	1.36	1.37	1.36	1.38
23-H	1.16s	1.20s	1.11s	1.16s
24-H	1.12s	0.70s	1.07s	1.10s
25-H	1.28s	0.90s	1.16s	1.19s
26-H	1.01s	0.96s	1.05s	1.06s
27-H	1.10s	1.19s	1.18s	1.16s
28-H	0.81s	0.81s	0.82s	0.83s
29-H	1.19s	1.20s	1.18s	1.21s



355



356





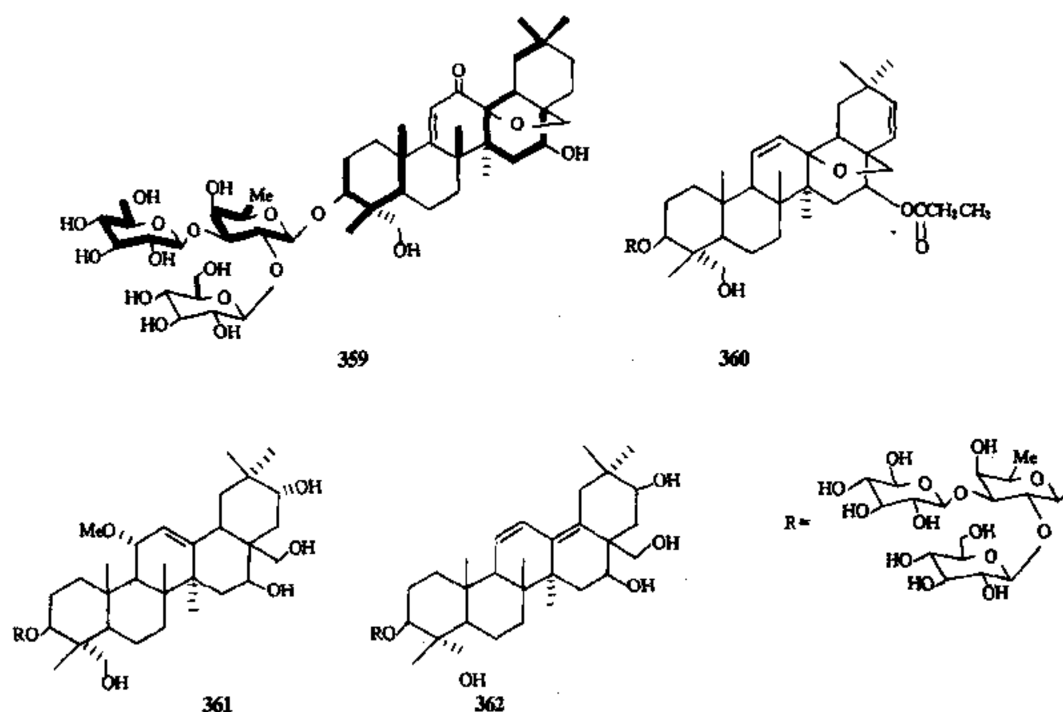
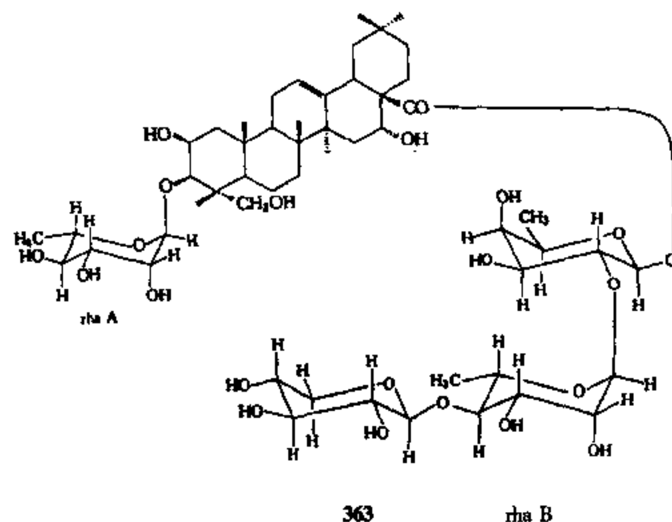


表 9-51 齐墩果烷衍生物 363 的 ^{1}H-NMR 化学位移[90]

甙元质子	δ	糖 体	糖体质子	δ
1-H_A	2.06	鼠李糖	1-H	4.91brs
1-H_B	1.23		2-H	3.95dd(1.6,3.3)
2-H	4.26d(3.3)		3-H	3.82d(3.3)
3-H	3.98d(3.7)		4-H	3.42t(9.5)
5-H	1.38		5-H	3.87
6-H_A	1.55		6-CH_3	1.29d(6.2)
6-H_B	1.49	木糖	1-H	4.54d(7.7)
7-H_A	1.68		2-H	3.30dd(7.7,6.4)
7-H_B	1.44		3-H	3.37
9-H	1.68		4-H	3.52ddd
11-H_A	2.03		5-H_A	3.91t(11)
11-H_B	1.97		5-H_B	3.91t(5.7)
12-H	5.36t(5.4)	鼠李糖	1-H	5.46d(1.7)
15-H_A	1.74dd(3.5,14.9)		2-H	3.97dd(1.7,3.9)
15-H_B	1.51dd(2.6,14.9)		3-H	3.89d(3.9)
16-H	4.53		4-H	3.58d(9.4)
18-H	2.98dd(4.2,14.3)		5-H	3.84
19-H_A	2.33t(13.7)		6-CH_3	1.36d(6.1)
19-H_B	1.07	岩藻糖	1-H	5.34d(8.2)
21-H_A	1.99		2-H	3.85
21-H_B	1.21		3-H	3.73
22-H_A	1.95		4-H	3.61d(3.4)
22-H_B	1.82dd(4.7,13.4)		5-H	3.73dd(3.4,6.4)
23-H_A	3.37		6-CH_3	1.27d(6.4)
23-H_B	3.28			
24-CH_3	0.94			
25-CH_3	1.36			
26-CH_3	0.87			
27-CH_3	1.43			
29-CH_3	0.92			
30-CH_3	0.99			

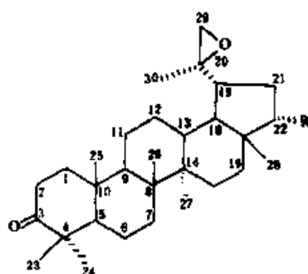


363

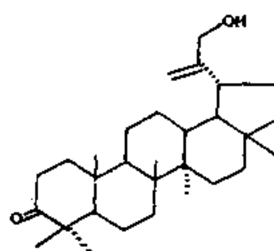
三、羽扇豆烷衍生物的^{1}H-NMR化学位移

表 9-52 羽扇豆烷衍生物 364～368 的^{1}H-NMR化学位移[62]

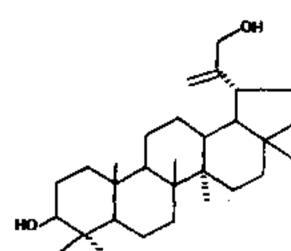
质子＼化合物	364	365	366	367	368	质子＼化合物	364	365	366	367	368
2-H_α	2.50ddd	2.52ddd	2.51ddd	2.50ddd	—	30-H	1.25s	1.25s	1.27s	4.13bs	4.13bs
2-H_β	2.41ddd	2.41ddd	2.42ddd	2.40ddd	—	CH_3	1.08s	1.08s	1.09s	1.08s	1.04s
3-H	—	—	—	—	3.20dd		1.07s	1.08s	1.08s	1.08s	0.97s
19-H	—	—	—	2.30ddd	2.29ddd		1.04s	1.04s	1.04s	1.03s	0.95s
21-H	—	2.13ddd	2.22ddd	—	—		0.96s	0.95s	0.96s	0.96s	0.83s
22-H	—	3.67dd	4.67dd	—	—		0.95s	0.94s	0.95s	0.93s	0.78s
29-H_A	2.66d	2.66d	2.66d	4.95bs	4.94bs		0.75s	0.78s	0.82s	0.80s	0.76s
29-H_B	2.61d	2.61bd	2.61bs	4.91bs	4.91bs						



364. R = H
365. R = OH
366. R = $OCOCH_3$



367

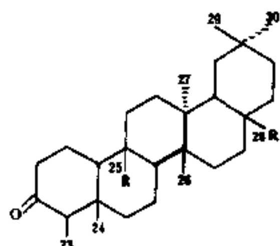


368

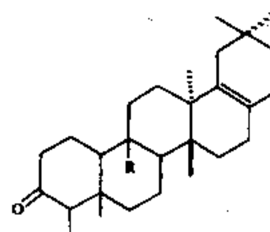
四、无羁萜烷衍生物的¹H-NMR化学位移

表 9-53 无羁萜烷衍生物 369~383 的¹H-NMR 化学位移[63]

化合物 \ 甲基	23	24	25	26	27	28	29	30
369	0.88	0.73	0.86	0.99	1.04	1.16	0.99	0.94
370	0.87	0.72	0.84	0.96	1.06	—	0.67	0.94
371	0.87	0.72	0.86	0.98	1.12	—	0.98	0.90
372	0.87	0.72	0.88	0.99	1.12	—	0.99	0.95
373	0.87	0.72	0.84	1.04	1.04	—	0.72	0.93
374	0.90	0.63	—	0.94	1.05	1.14	0.94	0.94
375	0.89	0.84	—	1.08	1.02	1.18	0.99	0.96
376	0.90	0.76	—	1.06	1.02	1.17	0.98	0.94
377	0.86	0.69	0.90	0.94	1.04	—	0.90	0.90
378	0.88	0.71	0.92	0.92	1.19	—	0.98	0.92
379	0.84	0.83	—	0.96	1.08	—	0.96	0.96
380	0.90	0.76	—	0.95	1.21	—	0.98	0.95
381	0.90	0.63	—	0.94	1.00	—	0.94	0.94
382	0.81	0.71	0.90	0.98	1.23	—	1.14	0.90
383	0.98	0.76	—	0.98	1.26	—	1.13	0.98



369. $R = R^1 = CH_3$
370. $R = CH_3$, $R^1 = CHO$
371. $R = CH_3$, $R^1 = CH_2OH$
372. $R = CH_3$, $R^1 = CH_2OCOH_3$
373. $R = CH_3$, $R^1 = CO_2CH_3$
374. $R = CHO$, $R^1 = CH_3$
375. $R = CH_2OH$, $R^1 = CH_3$
376. $R = CH_2OCOCH_3$, $R^1 = CH_3$
377. $R = CH_3$, $R^1 = OH$
378. $R = CH_3$, $R^1 = OCOCH_3$
379. $R = CH_2OH$, $R^1 = OH$
380. $R = CH_2OCOCH_3$, $R^1 = OCOCH_3$
381. $R = CHO$, $R^1 = OH$

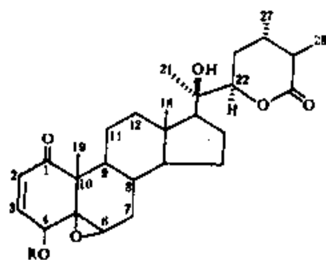


382. $R = CH_3$
383. $R = CH_2OCOCH_3$

五、其他三萜及甾体化合物的^{1}H-NMR化学位移

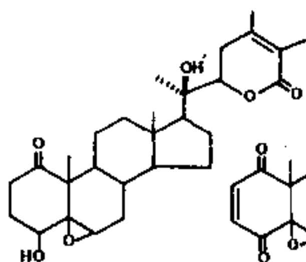
表 9-54　三萜及甾体化合物 384～393 的^{1}H-NMR 化学位移[64]

质子＼化合物	384	385	386	387	388	389	390	391	392	393
2-H	6.32d(10)	6.22d(10)	—	6.86s	6.85s	—	—	—	—	—
3-H	6.94dd (10,6)	7.02dd (10,6)	—	6.86s	6.85s	—	—	—	—	—
4-H	3.75d(6)	4.64d(6)	3.50t (3.2)	—	—	—	—	—	—	—
6-H	3.23bs	3.20 $W_{\frac{1}{2}}=4$	3.13bs	3.42d (2.3)	3.42d (2.3)	4.53m	4.50m	—	—	—
16-H	—	—	—	—	—	4.53m	4.50m	4.65m	4.66m	4.15ddd (7,7,7)
18-H	0.86s	0.85s	0.81s	0.88s	0.89s	0.76s	0.73s	0.82s	0.80s	0.86s
19-H	1.41s	1.39s	1.30s	1.38s	1.38s	0.90s	0.90s	0.98s	0.97s	0.96s
21-H	1.24s	1.24s	1.25s	1.28s	1.26s	1.03d(7)	1.06d(7)	0.98d(7)	0.93d(6)	1.05d(6)
22-H	4.17dd (11,3)	4.13m	4.20dd (13,5)	4.20dd	4.15m	—	—	—	—	—
23-H	—	—	—	—	—	4.83m	4.80m	—	—	—
26-H	—	—	—	—	—	3.50m	3.36d(11) 4.06dd (11,3)	3.40d(12) 4.25dd (12,3)	3.63m	3.72d(9)
27-H	1.22d(7)	1.20d(7)	1.97s	1.95s	1.22d (6.7)	0.76d(7)	1.19d(7)	1.07d(7)	0.93d(6)	0.96d(6)
28-H	1.14d (6.7)	1.14d (6.7)	1.87s	1.89s	1.14d (6.7)	—	—	—	—	—

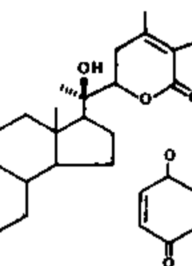


384. R = H

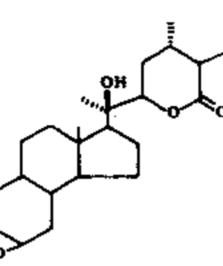
385. R = COCH$_3$



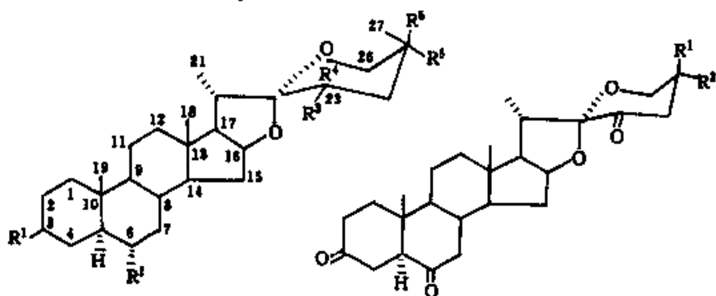
386

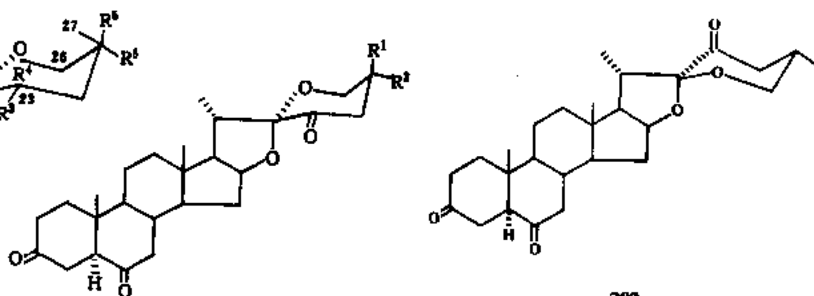


387



388





393

389. R^1 = R^2 = R^4 = OCOCH$_3$,
R^3 = R^5 = H, R^6 = CH$_3$

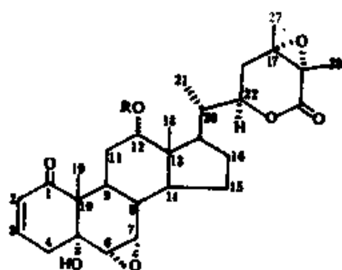
390. R^1 = R^2 = R^4 = OCOCH$_3$,
R^3 = R^6 = H, R^5 = CH$_3$

391. R^1 = CH$_3$, R^2 = H

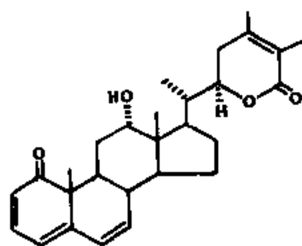
392. R^1 = H, R^2 = CH$_3$

表 9-55 三萜及甾体化合物 394～400 的 ^{1}H-NMR 化学位移[65,66]

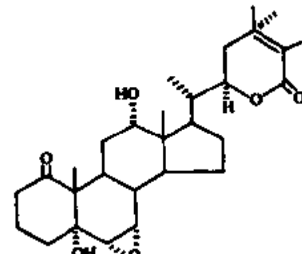
质子＼化合物	394	395	396	397	398	399	400
2-H	5.81dq (10,3,1)	5.81dq (10,3,1)	—	5.92d(9.5)	—	5.85d(10)	5.83dq (10,3,1)
3-H	6.60dq (10,5,3)	6.60dq (10,5,3)	—	6.99dd (9.5,5.5)	—	6.60dq (10,5,3)	6.54dq (10,5,3)
6-H	3.06d(4)	3.06d(4)	3.08d(4)	5.85d(10)	3.05d(4)	3.08d(4)	3.03d(4)
7-H	3.35d(4)	3.35d(4)	3.32d(4)	6.11dd (10,3)	3.28d(4)	3.42d(4)	3.30dd (4,1)
12-H	4.00m	5.08m	4.03m	4.09m	4.02m	—	—
18-H	0.88s	0.80s	0.74s	0.83s	0.76s	1.10s	0.75s
19-H	1.18s	1.21s	1.21s	1.25s	1.20s	1.26s	1.16s
21-H	1.02d(5)	1.02d(5)	1.02d(5)	1.08d(6)	1.10d(6)	0.90d(7)	0.92s
22-H	4.55m	4.55m	4.60m	4.38dt (12,4)	4.40dt (12,3)	4.58m	4.50dt (12,4)
27-H	1.50s	1.50s	1.80s	1.90s	1.91s	1.52s	1.48s
28-H	1.58s	1.58s	1.59s	1.95s	1.96s	1.58s	1.56s



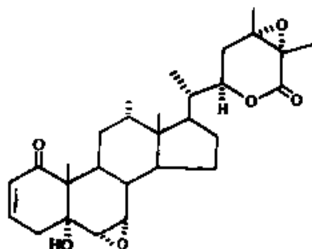
394. R = H
395. R = $COCH_3$
396. R = H,双键饱和



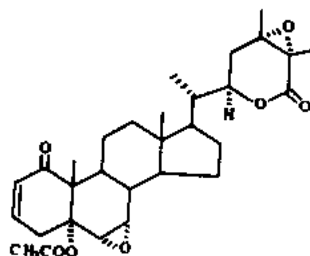
397



398



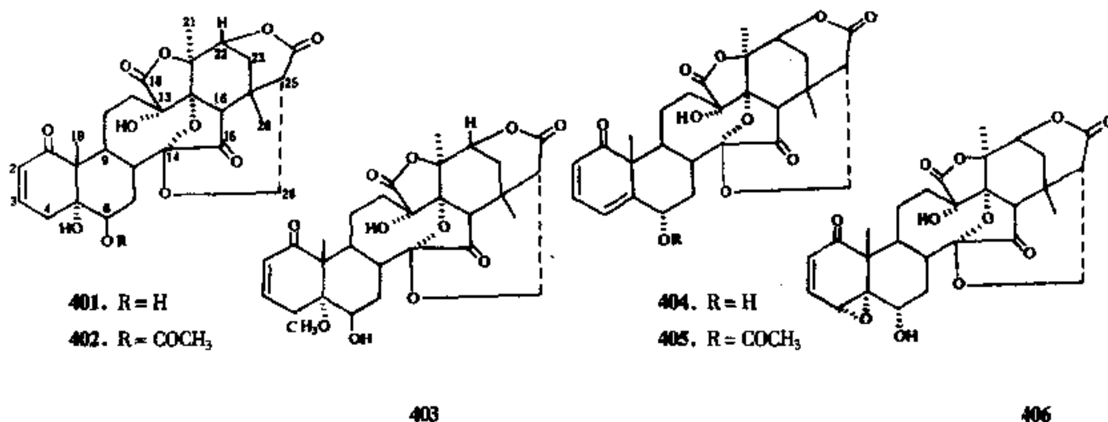
399



400

表 9-56 三萜及甾体化合物 401～406 的^{1}H-NMR 化学位移[67]

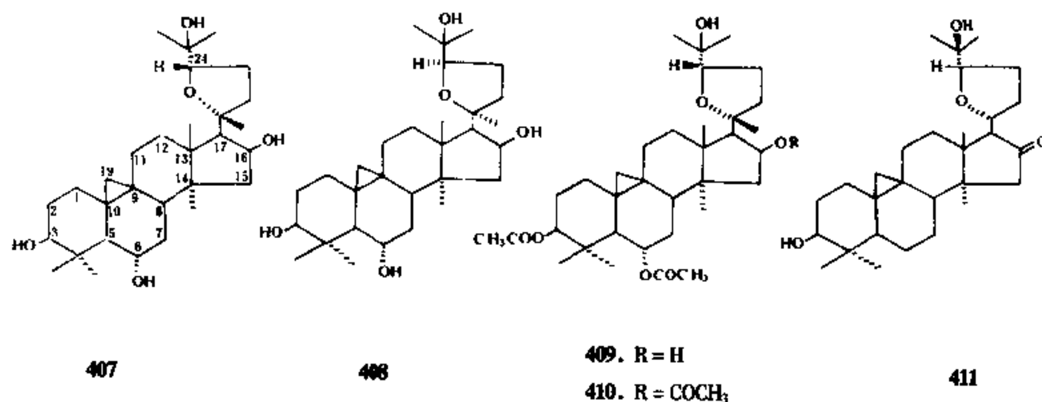
质子＼化合物	401	402	403	404	405	406
2-H	5.72dd(10,4)	5.72d(10)	5.91dd(10,3)	5.94d(10)	6.02d(10)	7.05dd(8,2)
3-H	6.61m(10)	6.63dm(10)	6.65dm(10)	7.04dd(10,6)	7.06dd(10,6)	6.73dd(8,6)
4-H	—	—	—	6.17d(6)	6.36d(6)	4.66dd(6,2)
6-H	3.85m	4.80m	3.84m	4.54m	5.50m	3.85m
7-H	—	—	—	—	4.54m	—
13-OH	5.68s	5.80s	5.70s	6.36s	—	6.54s
22-H	4.58m	4.56m	4.58m	4.54m	4.28dd	4.58m
26-H_A	4.2m	4.27dd(14,4)	4.29dd(14,4)	4.29dd(14,4)	3.60d(12)	4.30dd(12,4)
26-H_B	3.60d(14)	3.59d(14)	3.60d(13)	3.63d(13)	6.44d(13)	3.62d(12)
CH_3	1.83s	1.83s	1.84s	1.75s	1.72s	1.82s
	1.17s	1.17s	1.20s	1.26s	—	1.16s
	1.10s	1.13s	1.20s	1.20s	—	1.04s



401. R = H
402. R = $COCH_3$
403
404. R = H
405. R = $COCH_3$
406

表 9-57 三萜及甾体化合物 407～411 的^{1}H-NMR 化学位移[68]

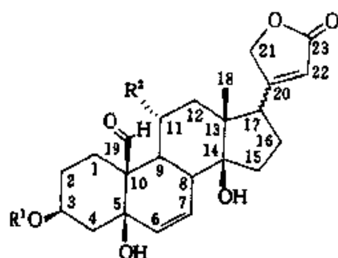
质子＼化合物	407	408	409	410	411
3-H	3.55q(4.8,1.2)	≈3.57m	≈4.5m	≈4.5m	≈4.68m
6-H	3.69ddd(4.9,9)	≈3.57m	≈4.6m	≈4.6m	≈4.68m
16-H	4.70ddd(ΣJ = 23)	4.90q(7)	≈4.5m	5.37m	—
19-H	0.22,0.50d(4.2)	0.23,0.51d(4)	0.30,0.57d(4.5)	0.30,0.55d(4.5)	0.43d(4.5)
24-H	3.83t(ΣJ = 15)	3.78q	3.74t	3.60t(ΣJ = 15)	3.78t(ΣJ = 15)
CH_3—	0.89,1.17	0.90,1.18	0.79,0.85	0.80,0.94	0.87,0.91
	1.23,1.24	1.20,1.25	0.94,1.06	0.94,1.08	0.96,1.16
	1.40,1.57	1.33,1.45	1.18,1.20	1.19,1.23	1.16,1.29
	1.78	1.78	1.34	1.29	1.16

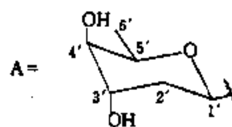


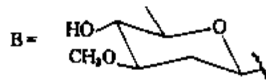
407　　408　　409. R = H　410. R = COCH$_3$　　411

表 9-58　三萜及甾体化合物 412～414 的^{1}H-NMR 化学位移[91]

质子＼化合物	412	413	414
1α-H(e)	2.84brdt(14,3)	2.09	2.05
1β-H(a)	2.61td(14,3)	2.47td(15,2.5)	2.47td(15,3)
2α-H(a)	2.51tt(14,13)	1.64brtt(14,≈2.5)	1.65brtt(14,≈2.5)
2β-H(e)	2.37brd quint(14,3)	2.23brd(14.5)	2.17brd(14)
3-H	4.42br quint(≈3)	4.34br quint(≈3)	4.33br quint(≈3)
4α-H(a)	2.07dd(15,3)	1.96	2.00
4β-H(e)	2.30brdt(15,3)	2.23brd(14.5)	2.35brd(14)
6-H	6.14dd(10.5,3)	6.05dd(10.5,2.5)	6.14dd(10,3)
7-H	6.37dd(10.5,2)	6.37brd(10.5)	6.40d(10)
8-H	2.76brdt(12.5,≈2)	2.61brd(12)	2.63brd(12)
9-H	2.50dd(12.5,8)	2.15brt(12)	2.16brt(12)
11α-H(e)	—	1.62ddd(13,3,2)	1.62
11β-H(a)	4.55	1.44brq(13)	1.44brq(13)
12α-H(a)	1.96	1.35td(13,3)	1.35td(13,3)
12β-H(e)	1.82dd(14.5,4.5)	1.49brd(13)	1.49brd(13)
15a-H	2.19	1.98	1.99
15b-H	1.94	1.82brt(9.5)	1.85brt(10)
16a-H	2.02	2.08	2.10
16b-H	1.80		
17-H	3.46dd(9.5,6.5)	2.77dd(8,6)	2.77dd(8,6)
18-H	1.02s	0.96s	0.96s
19-H	10.46	10.37s	10.39s
21a-H	5.12d(2)	5.25dd(18,1.5)	5.25dd(18,1.5)
21b-H		5.02dd(18,1.5)	5.02dd(18,1.5)
22-H	6.12brs	6.15brs	6.12brs
1′-H	5.45dd(10,3)	5.43dd(10,3)	4.80dd(9.5,2)
2′α-H	2.41ddd(13.5,10,3)	2.39ddd(13.5,10,3)	1.59
2′β-H	2.12dt(13.5,3)	2.11	2.38brd,(≈13)
3′-H	4.57brq(3)	4.57brq(3)	3.36td(9,5)
4′-H	3.78brdd(3,1)	3.79brdd(3,1)	3.44t(9)
5′-H	4.46qd(6.5,1)	4.46qd(6.5,1)	3.51dq(9,6)
6′-H	1.46d(6.5)	1.51d(6.5)	1.52d(6)
3′-OMe	—	—	3.43s







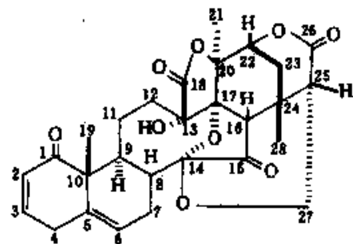
412. R^1 = A; R^2 = OH; 17β-H

413. R^1 = A; R^2 = H; 17α-H

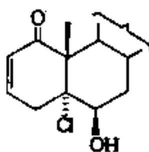
414. R^1 = B; R^2 = H; 17α-H

表 9-59 三萜及甾体化合物 415 ~ 417 的 ^{1}H-NMR 化学位移[92]

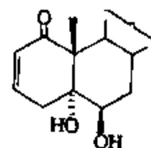
质子＼化合物	415	416	417
2-H	5.80dd	5.83dd	5.70dd
	($J_{2,3}=10$)	($J_{2,3}=10$)	($J_{2,3}=10$)
	($J_{2,4\beta}=2$)	($J_{2,4\beta}=2.5$)	($J_{2,4\beta}=2$)
3-H	6.89ddd	6.78ddd	6.62ddd
	($J_{3,2}=10$)	($J_{3,2}=10$)	($J_{3,2}=10$)
	($J_{34\alpha}=5$)	($J_{3,4\alpha}=5$)	($J_{3,4\alpha}=5$)
	($J_{3,4\beta}=2$)	($J_{3,4\beta}=2$)	($J_{3,4\beta}=2$)
4-H	2.89dd(α)	2.46dd(α)	1.98dd(α)
	($J_{4\alpha,4\beta}=20$)	($J_{4\alpha,4\beta}=21$)	($J_{4\alpha,4\beta}=20$)
	($J_{4\alpha,3}=5$)	($J_{4\alpha,3}=5$)	($J_{4\alpha,3}=5$)
	3.27br d(β)	3.48ddd(β)	3.11br d(β)
	($J_{4\alpha,4\beta}=20$)	($J_{4\alpha,4\beta}=21$)	($J_{4\alpha,4\beta}=20$)
		($J_{4\beta,2}=2.5$)	
		($J_{4\beta,3}=2$)	
5-H			4.25s(OH)
6-H	5.59br d	3.88dt	3.49m
	($J_{6,7\beta}=6$)	($J_{6,OH}=5$)	($W_{h/2}=11$)
		($J_{6,7\alpha}=3$)	
		($J_{6,7\beta}=3$)	
		5.66d(OH)	4.90d(OH)
		($J_{OH,6}=5$)	($J_{OH,6}=4$)
7-H	1.97m(α)	1.95m(α)	—
	2.21m(β)	2.04m(β)	—
8-H	1.92m	2.27dt	2.20dt
		($J_{8,9}=11.5$)	($J_{8,9}=11$)
		($J_{8,7\alpha}=11.5$)	($J_{8,7\alpha}=11$)
		($J_{8,7\beta}=4$)	($J_{8,7\beta}=5$)
9-H	2.95dd	3.35dd	3.11m
	($J_{9,8}=11$)	($J_{9,8}=11.5$)	
	($J_{9,11\beta}=9$)	($J_{9,11\beta}=8$)	
11-H	2.18m(α)	2.13m(α)	—
	1.10m(β)	0.97m(β)	0.94m(β)
12-H	2.17m(α)	1.89m(α)	2.11m(α)
	1.45m(β)	1.44br dd(β)	1.45dd(β)
	($J_{12\beta,12\alpha}=16$)	($J_{12\beta,12\alpha}=16$)	($J_{12\beta,12\alpha}=16$)
	($J_{12\beta,11\beta}=9$)	($J_{12\beta,11\beta}=9$)	($J_{12\beta,11\beta}=10$)
13-H	6.28s(OH)	6.06s(OH)	5.76s(OH)
16-H	2.86s	2.82s	2.77s
19-H	1.09s(Me)	1.24s(Me)	1.11s(Me)
21-H	1.78s(Me)	1.81s(Me)	1.81s(Me)
22-H	4.56dd	4.57dd	4.56dd
	($J_{22,23R}=3$)	($J_{22,23R}=3$)	($J_{22,23R}=3$)
	($J_{22,23S}=2$)	($J_{22,23S}=2$)	($J_{22,23S}=2$)
23-H	1.96m(S)	1.93dd(S)	1.93br d(S)
		($J_{23S,23R}=15$)	($J_{23S,23R}=14$)
		($J_{23S,22}=2$)	
	2.14m(R)	2.10dd(R)	2.10dd(R)
		($J_{23R,23S}=15$)	($J_{23R,23S}=14$)
		($J_{23R,22}=3$)	($J_{23R,22}=4$)
25-H	2.88br d	2.89dd	2.87d
	($J_{25,27S}=4$)	($J_{25,27S}=4.5$)	($J_{25,27S}=4$)
		($J_{25,27R}=1$)	
27-H	3.60dd(R)	3.59dd(R)	3.58d(R)
	($J_{27R,27S}=14$)	($J_{27R,27S}=13$)	($J_{27R,27S}=13$)
	($J_{27R,25}=1$)	($J_{27R,25}=1$)	
	4.26dd(S)	4.26dd(S)	4.25dd(S)
	($J_{27S,27R}=14$)	($J_{25S,27R}=13$)	($J_{27S,27R}=13$)
	($J_{27S,25}=4$)	($J_{27S,25}=4.5$)	($J_{27S,25}=4$)
28-H	1.16s(Me)	1.17s(Me)	1.17s(Me)



415



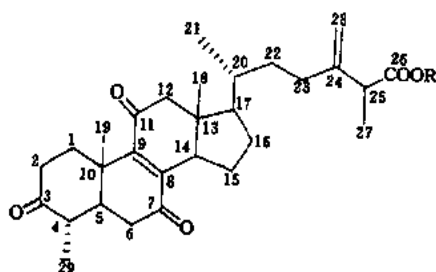
416



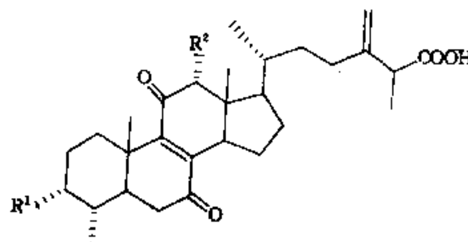
417

表 9-60　三萜及甾体化合物 418～420 的^{1}H-NMR 化学位移[93]

质子＼化合物	418	419	420	质子＼化合物	418	419	420
1α-H	1.40m	1.40m	1.35m	15-H	1.40m,2.45m	1.40m,2.50m	1.42m,2.50m
1β-H	3.04ddd(2.7, 6.6,13.4)	2.50m	2.22m	16-H	1.20m,2.00m	1.25m,1.98m	1.25m,1.95m
				17-H	1.40m	1.40m	1.85m
2-H	2.48m,2.50m	1.70m,1.80m	1.75m	18-H	0.66s	0.65s	0.61s
3-H		3.78brs	3.76brs	19-H	1.50s	1.29s	1.26s
4-H	2.42m	1.72m	1.70m	20-H	1.40m	1.40m	1.42m
5-H	1.88td(12.7, 4.3)	2.13td(10.8, 4.3)	2.03m	21-H	0.90d(5.4)	0.91d(5.3)	0.92d(6.3)
				22-H	1.18m,1.55m	1.18m,1.56m	1.15m,1.55m
6α-H	2.43m	2.39dd(15, 4.3)	2.40m	23-H	1.95m,2.18m	1.95m,2.16m	1.87m,2.15m
				25-H	3.11q(7.0)	3.13q(7.0)	3.16q(7.0)
6β-H	2.46m	2.23t(15)	2.22m	27-H	1.26d(7.0)	1.28d(7.0)	1.28d(7.0)
12α-H	2.37brd(14)	2.39brd(14)		28b-H	4.94brs	4.96brs	4.95brs
12β-H	2.91d(14)	2.87d(14)	4.02s	28a-H	4.88d(2.6)	4.94brs	4.90brs
14-H	2.63dd(7.3, 11.9)	2.60dd(11.8, 7.3)	2.98dd(12.2, 7.4)	29-H	1.01d(6.5)	0.94d(6.8)	0.91d(6.5)



418. R = H



419. R^1 = OH, R^2 = H

420. R^1 = R^2 = OH

表 9-61　三萜及甾体化合物 421～423 的^{1}H-NMR 化学位移[94]

质子＼化合物	421	422	423	质子＼化合物	421	422	423
1-H	2.12brd (14.5)	2.12brd (14.5)	2.12brd (14.5)	18-H	0.72s	0.72s	0.72s
	1.50dd (14.5,4)	1.50dd (14.5,4)	1.50dd (14.5,4)	19-H	1.09s	1.09s	1.09s
				20-H	1.40m		
				21-H	0.97d(6.6)	0.98d(7)	0.98d(7)
2-H	4.84brs	4.84brs	4.84brs	22-H	0.91m		
3-H	4.78brs	4.78brs	4.78brs	23-H	1.65m		
4-H	2.32brd(15)	2.32brd(15)	2.32brd(15)	24-H	1.14m		
	1.83dt (15,2.7)	1.83dt (15,2.7)	1.83dt (15,2.7)	26-H	1.28q(7)	0.83d(7)	4.72brs
				27-H	0.82s	0.83d(7)	1.67s
5-H	1.68dt (2.7,11.2)	1.68dt (2.7,11.2)	1.68dt (2.7,11.2)	28-H	0.85d(6.5)	0.91d(7)	1.03d(7)
				29-H	0.83s	—	—
6-H	4.22dt (4.4,11.2)	4.22dt (4.4,11.2)	4.22dt (4.4,11.2)	30-H	0.84t(7)	—	—
7-H	2.40dt (4.4,12.2)	2.40 (4.4,12.2)	2.40dt (4.4,12.2)				

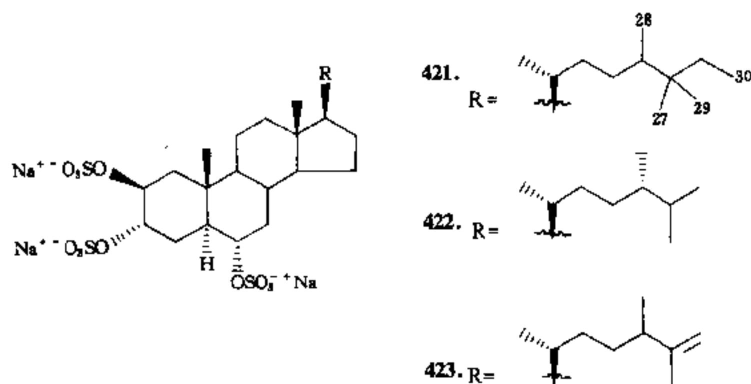
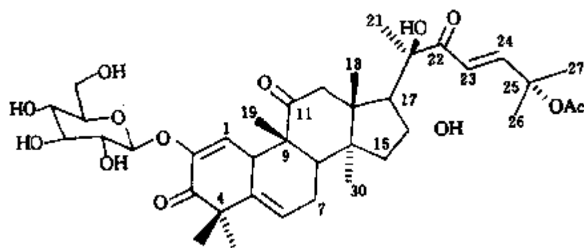
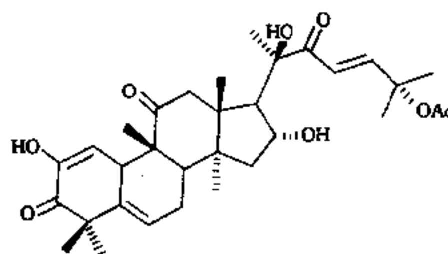


表 9-62　三萜及甾体化合物 424～428 的^{1}H-NMR 化学位移[95]

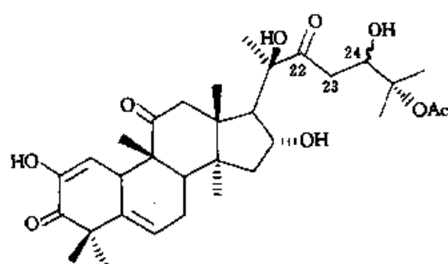
质子 \ 化合物	424	425	426	427	428
1-H	6.10d(2)	5.93d(2)	5.93d(2)	5.93d(2)	5.91d(2)
6-H	5.83brs	6.75brs	5.76brs	5.77brs	5.76brs
7α-H	2.41m	2.43m	2.42m	2.37m	2.36m
7β-H	2.13	2.10	2.18	2.20	2.17
8-H	2.09d(8)	2.05d(8)	2.05d(8)	2.04d(8)	1.99d(8)
10-H	3.69brs	3.51brs	3.50brs	3.51brs	3.51brs
12α-H	3.40d(14)	3.21d(14)	3.26d(14)	3.21d(14)	3.23d(14)
12β-H	2.57d(14)	2.70d(14)	2.69d(14)	2.69d(14)	2.70d(14)
15α-H	1.88	1.95	1.90	1.88	1.91
15β-H	1.46	1.70	1.52	1.51	1.59
16-H	4.54t(7)	4.39t(7)	4.39t(7)	4.46t(7)	4.51brt
17-H	2.62d(7)	2.95d(7)	3.04d(7)	3.08d(7)	3.06d(7)
18-H	0.89	0.98	1.00	0.99	0.97
19-H	1.41	1.41	1.03	1.02	1.01
21-H	1.41	1.34	1.43	1.41	1.20
23-H	6.82d(15)	6.46d(15)	2.58br	2.62br	3.46br
24-H	6.98d(15)	7.04d(15)	4.16brt	4.06brt	ND
26-H	1.57	1.55	1.25	1.25	1.24
27-H	1.54	1.56	1.47	1.45	1.30
28-H	1.30	1.38	1.35	1.35	1.33
29-H	1.27	1.26	1.24	1.26	1.35
30-H	1.01	1.02	1.41	1.40	1.39
OAc-H	2.01	2.00	1.90	1.91	1.95
1'-H	4.69d(7)	—	—	—	—



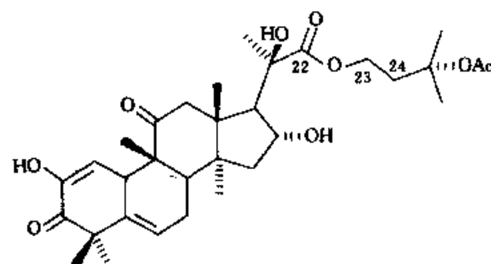
424



425



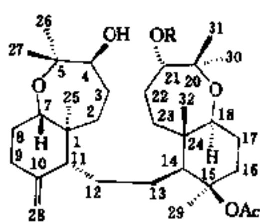
426, 427



428

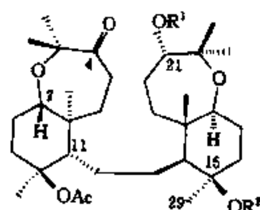
表 9-63 三萜及甾体化合物 429 ~ 437 的^{1}H-NMR 化学位移[96]

质子 \ 化合物	429	430	431	432	433	434	435	436	437
2-H	1.48	1.49	1.59	1.32	1.33	1.32	1.26	1.31	1.29
	1.65	1.66	nd	1.87	1.87	1.80	1.41	1.80	1.79
3-H	1.82	1.79	1.74	2.13	2.13	2.13	1.75	2.13	2.14
	2.00	1.98	2.02	3.18	3.18	3.20	2.00	3.19	3.20
4-H	3.83	3.82	3.82	—	—	—	4.99	—	—
7-H	3.68	3.67	3.63	2.97	2.97	2.96	3.48	2.95	2.92
8-H	1.38	1.36	1.43	1.33	1.36	1.27	1.41	1.30	—
	1.62	1.63	1.53	1.61	1.56	1.58	1.57	1.61	—
9-H	1.95	1.95	1.66	1.67	1.69	1.62	1.66	1.67	1.79
	2.24	2.25	2.63	2.65	2.67	2.68	2.66	2.66	
11-H	1.64	1.66	1.53	1.46	1.45	1.42	1.47	1.43	1.00
12-H	1.50	1.52	1.47	—	—	—	1.34	—	1.29
	1.62	1.68	—	1.60	1.62	1.60	1.57	1.60	1.54
13-H	1.18	1.12	—	1.35	1.30	1.33	1.38	na	1.29
	1.72	1.68	1.77	1.74	1.69	1.70	1.75	1.74	1.75
14-H	0.74	0.83	0.80	0.79	0.83	0.74	0.76	0.69	0.66
16-H	1.31	1.26	1.26	1.26	1.47	1.45	1.47	1.45	1.23
	2.80	2.76	2.78	2.78	1.60	1.61	1.64	1.64	2.84
17-H	1.39	1.36	1.36	1.37	1.39	1.40	1.41	1.45	1.47
	1.51	1.43	1.46	1.46	1.71	1.74	1.73	1.88	1.60
18-H	3.41	3.55	3.56	3.55	3.50	3.35	3.37	2.89	2.93
21-H	4.97	3.82	3.82	3.83	3.82	4.97	4.98	—	—
22-H	1.81	1.75	1.74	1.74	1.73	1.76	1.75	2.09	2.12
	2.00	1.98	2.02	2.03	2.02	1.98	2.00	3.23	3.23
23-H	1.27	1.38	1.45	1.38	1.37	1.22	1.26	1.17	1.20
	1.45	1.57	1.69	1.56	1.53	1.60	1.41	1.80	1.79
25-H_3	0.70	0.69	0.83	0.98	0.99	0.99	0.87	0.96	0.93
26-H_3	1.12	1.12	1.11	1.25	1.25	1.25	1.20	1.27	1.27
27-H_3	1.27	1.26	1.26	1.31	1.31	1.31	1.14	1.30	1.31
28-H_3	4.60	4.61	1.48	1.50	1.50	1.50	1.50	1.50	1.18
	4.89	4.88	—	—	—	—	—	—	—
29-H_3	1.53	1.51	1.53	1.52	1.17	1.20	1.24	1.18	1.53
30-H_3	1.15	1.27	1.27	1.26	1.27	1.15	1.15	1.31	1.30
31-H_3	1.20	1.11	1.13	1.14	1.13	1.20	1.18	1.25	1.26
32-H_3	0.94	0.93	0.96	0.94	0.99	0.97	1.00	1.12	1.08
4-$OCOCH_3$	—	—	—	—	—	—	2.15	—	—
10-$OCOCH_3$	—	—	1.89	1.90	1.97	1.96	1.98	1.96	—
15-$OCOCH_3$	1.95	1.93	1.93	1.93	—	—	—	—	1.96
21-$OCOCH_3$	2.17	—	—	—	—	2.15	2.16	—	—



429. R = Ac

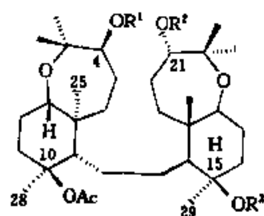
430. R = H



432. R^1 = H, R^2 = Ac

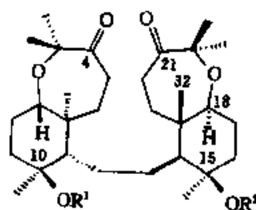
433. R^1 = H, R^2 = H

434. R^1 = Ac, R^2 = H



431. R^1 = H, R^2 = H, R^3 = Ac

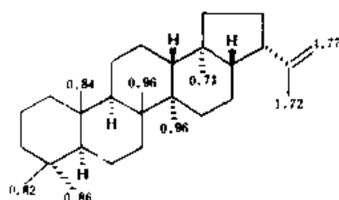
435. R^1 = Ac, R^2 = Ac, R^3 = H



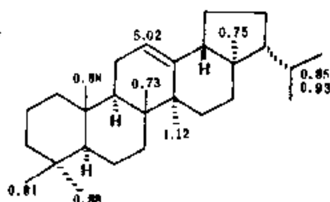
436. R^1 = Ac, R^2 = H

437. R^1 = H, R^2 = Ac

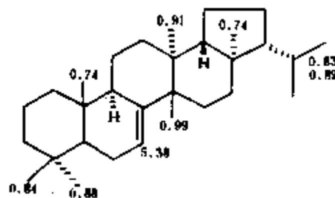
六、少数不同类型三萜及甾体化合物438～470的^{1}H-NMR化学位移



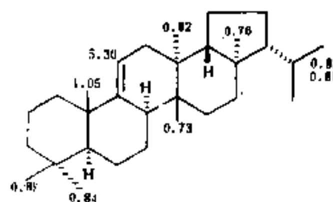
438[57]



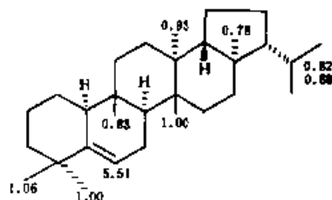
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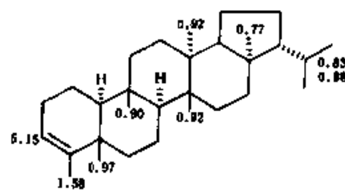
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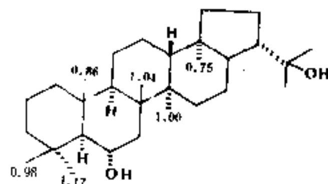
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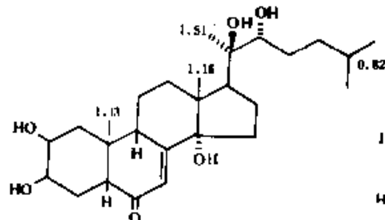
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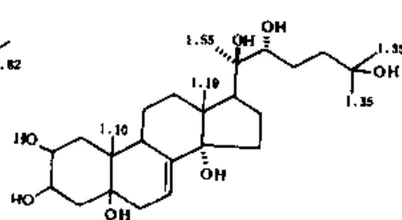
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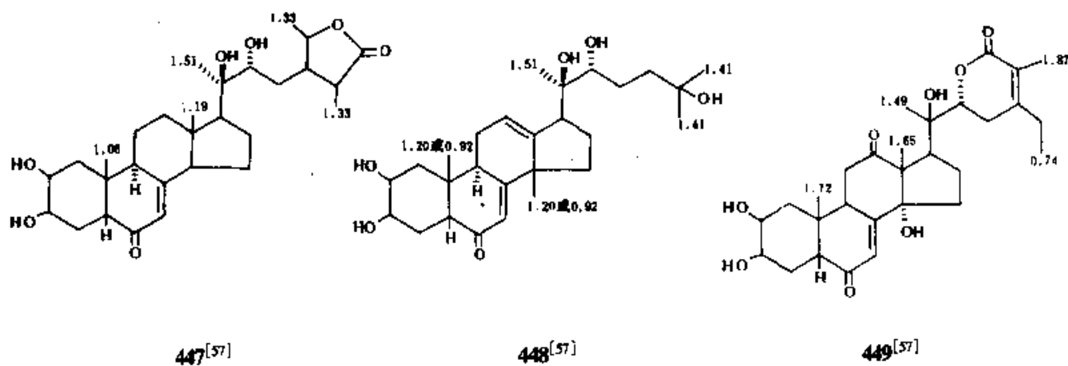
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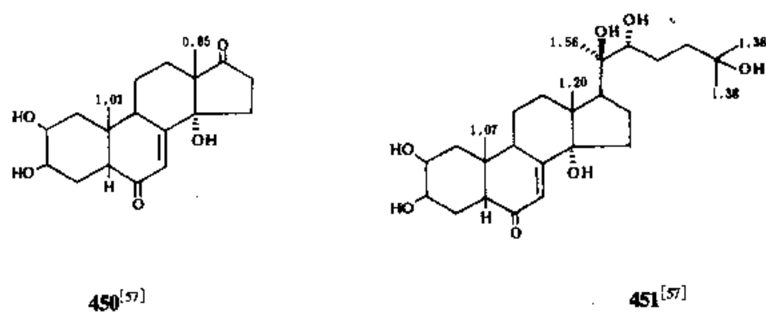
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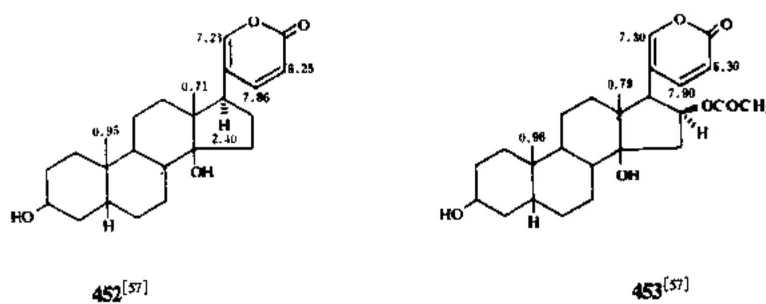
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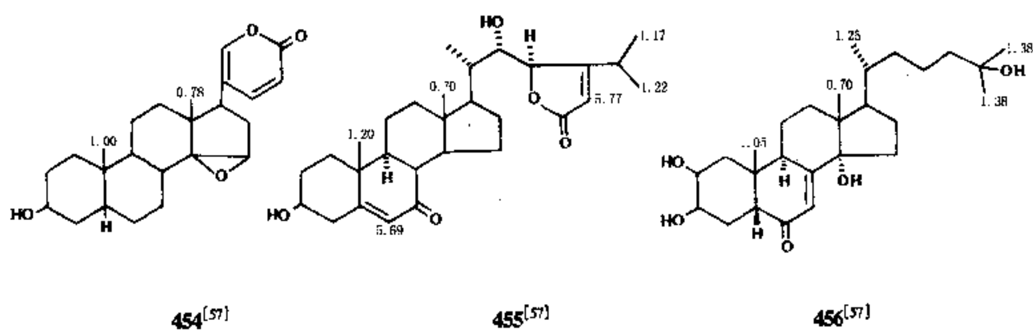
447[57]　　448[57]　　449[57]



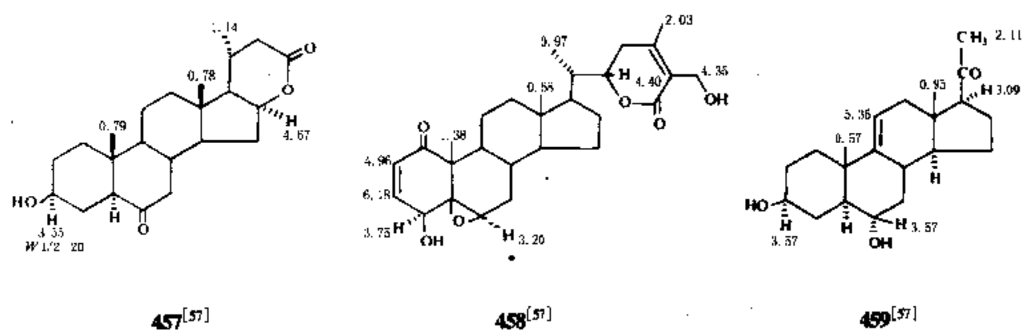
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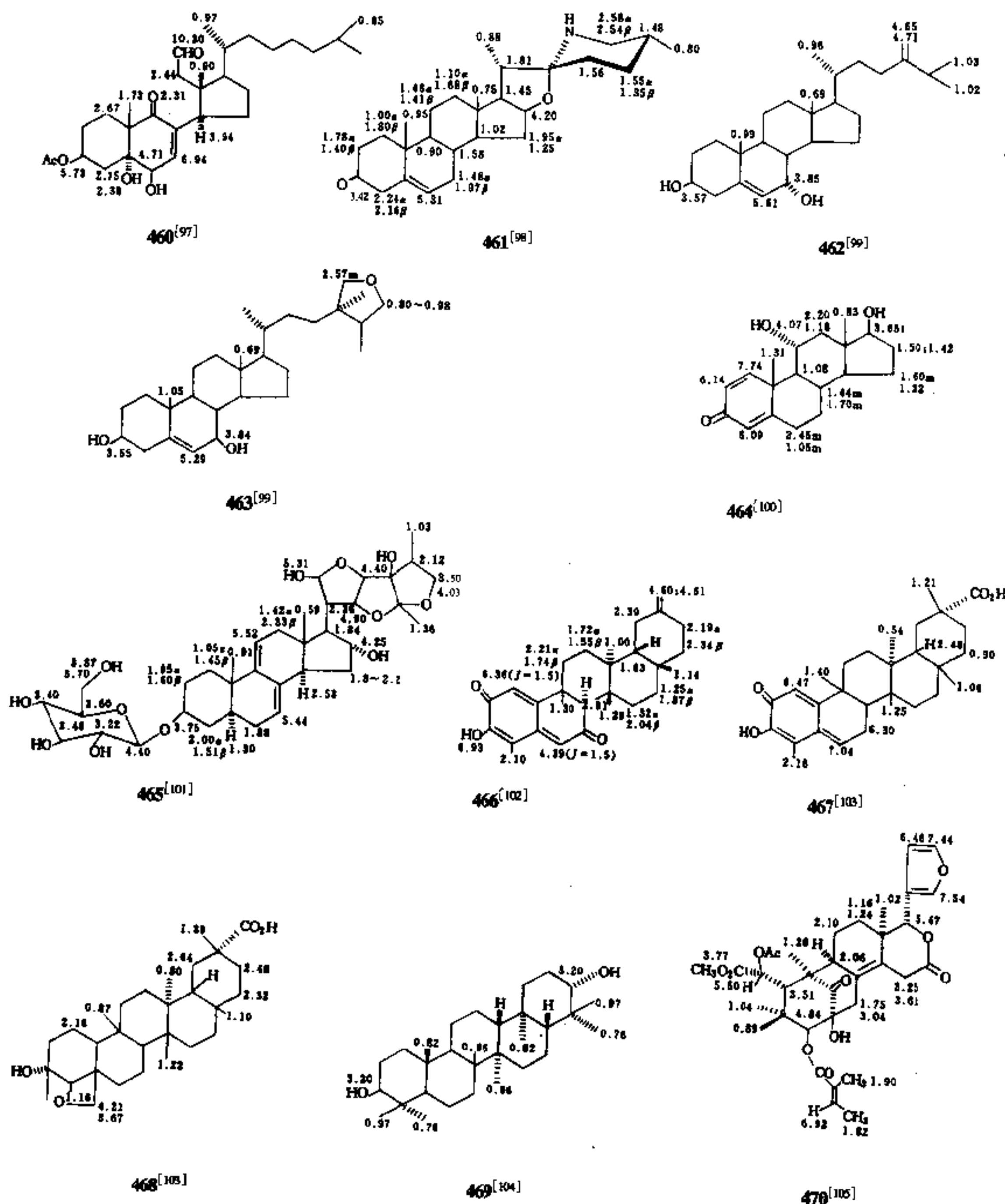
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454[57]　　455[57]　　456[57]



457[57]　　458[57]　　459[57]



460[97] 461[98] 462[99] 463[99] 464[100] 465[101] 466[102] 467[103] 468[103] 469[104] 470[105]

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第十章 香豆素及醌类化合物的 ^{1}H-NMR 化学位移和偶合常数

第一节 香豆素类化合物的^{1}H-NMR 化学位移和偶合常数

一、简单香豆素化合物的^{1}H-NMR 化学位移

表 10-1 简单香豆素化合物 1~7 的^{1}H-NMR 化学位移①

化合物＼质子	3-H	4-H	5-H	6-H	8-H	CH_3O	HO
1	6.11	7.83	7.42d(8.5)	6.68d(8.5) d(2.5)	6.62d(2.5)		HO:10.2
2	6.17	7.58	7.32d(8.5)	6.78d(8.5) d(2.5)	6.72d(2.5)	CH_3O:3.82	
3	6.14	7.84	6.96s	—	6.73s		6-HO:8.9, 7-HO:10.2
4	6.18	7.87	7.18s	—	6.75s	CH_3O:3.80	HO:10.2
5	6.25	7.58	7.24s	—	6.82s	CH_3O_2':3.89,3.92	
6	6.16	7.98	6.99d(8.5)	6.77d(8.5)			8-HO:9.3 7-HO:10.1
7	6.11	7.93	—	6.26d(2.5)	6.37d(2.5)	CH_3O_2':3.83,3.88	

① 除标明外，所有数据皆用 $CDCl_3$ 为溶剂；H_3 和 H_4 皆为双峰，J=9.5~10.0；括号内数字为 J 值。

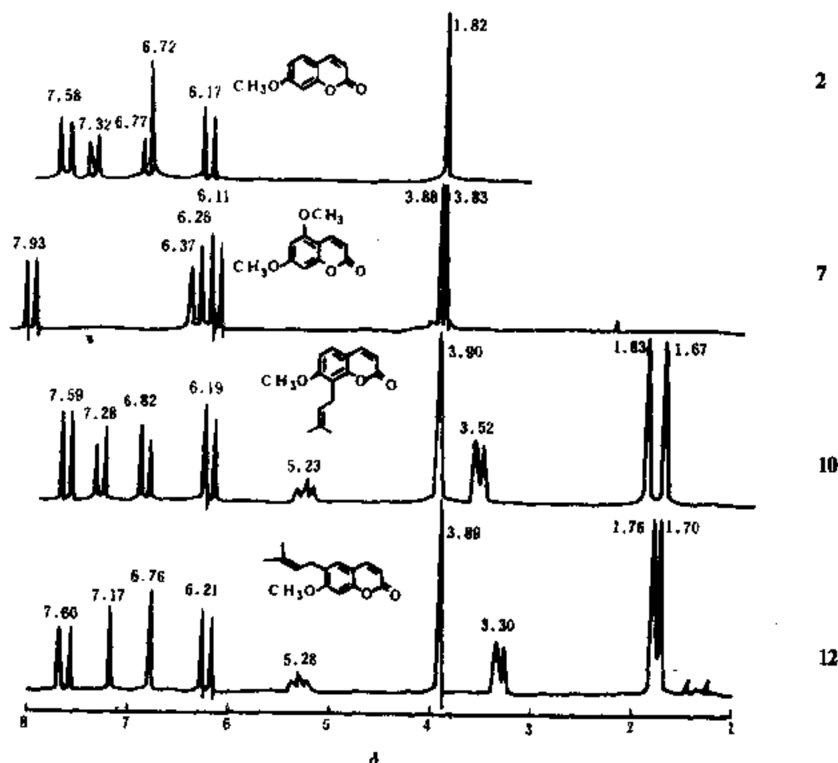


图 10-1 化合物 **2**、**7**、**10** 及 **12** 的^{1}H-NMR 图 100MHz 溶剂为 $CDCl_3$

二、6,8-双烯基取代香豆素化合物的¹H-NMR化学位移和偶合常数

表 10-2 3-甲基-2-丁烯基取代的香豆素(8～14,24～26)的¹H-NMR化学位移和偶合常数①

质子 化合物	3-H	4-H	5-H	6-H或8-H	五碳侧链 a-H	五碳侧链 b-H	五碳侧链 CH_3	OCH_3	OH	呋喃环 a-H	呋喃环 b-H	文献
8	6.28	7.57	7.31d(g)	6.78m	4.54d(7)	5.43t(7) q(1)	1.76s 1.80d(1)	—	—	—	—	—
9	6.23	7.65	7.20s	7.07s	3.38d(7)	5.34t(7) q(1)	1.76s 1.80d(1)	—	7.44s	—	—	—
10	6.21	7.60	7.17s	6.76s	3.30d(7)	5.28t(7) q(1)	1.70s 1.76d(1)	3.89s	—	—	—	—
11	6.23	7.60	7.22d(8.5)	6.70d(8.5)	3.61d(7)	5.27t(7) q(1)	1.75d(1) 1.86s	—	6.34s	—	—	—
12	6.19	7.59	7.28d(8.5)	6.82d(8.5)	3.52d(7)	5.23t(7) q(1)	1.67d(1) 1.83s	3.90s	—	—	—	—
13	6.21	7.52	6.91s	6.76s	4.61d(7)	5.42t(7) q(1)	1.76(s) 1.78d(1)	—	5.9s	—	—	—
14	6.09	7.94	—	6.29s	3.41d(7)	5.18t(7) q(1)	1.64d(1) 1.80s	3.90s	—	—	—	—
24	6.32	7.71	7.31s	—	4.37d(7)	5.58t(7) q(1)	1.74d(1)	—	—	6.77d(2)	7.64d(2)	—
23	6.21	8.11	—	7.09d(1)	4.88d(7)	5.52t(7) q(1)	1.69d(1) 1.79s	—	—	6.92d(2) d(1)	7.55d(2)	—
26	6.22	8.06	—	—	4.81d(7)	5.58t(7) q(1)	1.69s	4.15s	—	6.96d(2)	7.59d(2)	—
25	6.26	8.15	—	—					—	6.93d(2)	7.62d(2)	1

① 表中括号内的数字为偶合常数值。

表 10-3 3-甲基-2-丁烯基侧链含氧取代香豆素(15,17,18,27～30)的¹H-NMR化学位移和偶合常数①

质子 化合物	3-H	4-H	5-H	6-H或8-H	五碳侧链 a-H	五碳侧链 b-H	五碳侧链 CH_3	OCH_3	呋喃环 a-H	呋喃环 b-H	文献
15	6.23	7.62	7.35d(9)	6.86d(9)	3.1m		1.28,1.48s	3.93s	—	—	—
17	6.10	7.95	—	6.35s	3.0m		1.27,1.46s	3.92s	—	—	—
30	6.35	8.08	—	—	2.8～3.5m		1.30,1.49s	4.22s	6.89d(2)	7.67d(2)	2
27	6.22	8.12d(1)	—	7.05t(1)	4.36d(6.5)d(11) 3.20d(4)d(6.5) 4.60d(4)d(11)		1.33,1.40s	—	6.92d(2)d(1)	7.57d(2)	—
29	6.35	7.77	7.40s	—	4.57d(5.5) 3.30t(5.5)		1.28,1.34s	—	6.83d(2)	7.69d(2)	—
18	6.10	7.98	—	6.32s	2.90t	3.58q	1.30s	3.92s	—	—	3
28	6.15	8.10	—	7.01d(1)	4.37d(7.5)d(9) 3.87d(3.5)d(7.5) 4.53d(3.5)d(9)		1.30,1.34s	—	6.93d(2)d(1)	7.53d(2)	—

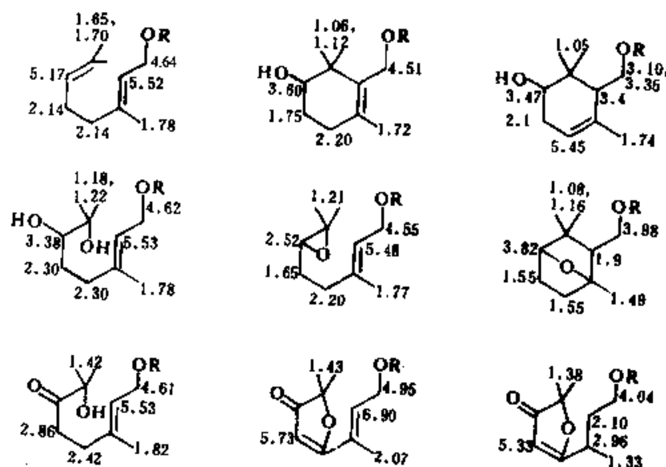
① 表中括号内的数字为偶合常数值。

表 10-4 其他五碳侧链取代香豆素 40～51 的¹H-NMR 化学位移

质子 / 化合物	a-H	b-H	c-H	CH_3	$=CH_2$	文献
40	4.17dd	3.20d	—	1.75dd	5.03m	2
					5.15m	
41	—	6.4dd	—	1.70[6H]	4.99dd,5.01dd	4
42	—	3.8m	1.6～1.8m	1.18d 0.92t	—	5
43	—	3.00d	2.2m	0.98d[6H]	—	5
44	3.10dd	4.30dd	—	1.83s	4.80d	6
45	≈4.35m	—	—	1.71s	4.86s	7
					5.06s	
46	4.00s	—	2.81m	1.21d	—	
47	3.32oct	5.37t	—	1.76s	5.03s	8
48	6.88d	6.32d	—	1.44s[6H]	—	9
49	—	6.00～6.45m	—	1.65s[6H]	4.70m	10
					4.95m	
50	—	6.17～6.67m	—	1.77s[6H]	4.81m,5.15m	10
51	—	6.15d	—	1.69s[6H]	4.98m	11

三、7-羟基香豆素的香叶烷基倍半萜衍生物的¹H-NMR 化学位移

7-羟基香豆素的香叶烷基衍生物的化学位移如下：



R＝7-香豆素

四、呋喃及吡喃香豆素化合物的^{1}H-NMR化学位移和偶合常数

表 10-5 简单呋喃及吡喃香豆素 19～51 的^{1}H-NMR 化学位移和偶合常数①

化合物＼质子	3-H	4-H	5-H	6-H 或 8-H	a-H	b-H	OCH$_3$	文献
呋喃香豆素								
19	6.33	7.75	7.64s	7.41d[1]	6.79d(2.5)d(1)	7.65d(2.5)	—	—
20	6.32	7.72	7.31s	—	6.78d(2.5)	7.65d(2.5)	4.25	—
21	6.25	8.14	—	7.12d(1)	7.02d(2.5)d(1)	7.59d(2.5)	4.25	—
22	6.25	8.08	—	—	6.96d(2.5)	7.59d(2.5)	4.14[6H]	—
31	6.36	7.78	7.36d(8.7)	7.42d(8.7)d(1)	7.12d(2.5)d(1)	7.67d(2.5)	—	—
32	6.27	8.11	—	6.58d(1)	6.99d(2.5)d(1)	7.54d(2.5)	3.95	—
33	6.38	7.75	6.78s	—	7.12d(2.5)	7.70d(2.5)	4.04	—
34	6.36	8.11	—	—	7.08d(2.5)	7.65d(2.5)	4.04,4.14	—
吡喃香豆素								
35	6.19	7.56	7.03s	6.71s	6.33d(10)	5.67d(10)	1.46[6H]	—
36	6.18	7.83	—	6.52 < 1	6.57d(10)d(1)	5.69d(10)	3.85;1.45[6H]	—
37	6.21	7.60	6.86s	—	6.35d(10)	5.31d(10)		12
38	6.19	7.57	7.18d(9)	6.59d(9)d(1)	6.86d(10)d(1)	5.70d(10)	1.46[6H]	—
39	6.20	7.56	6.78s	—	6.80d(10)	5.73d(10)		13
51	6.15	7.9	—	—	6.6d(10)	5.75d(10)	3.85;1.48[6H]	11

① 表中括号内的数字为偶合常数。

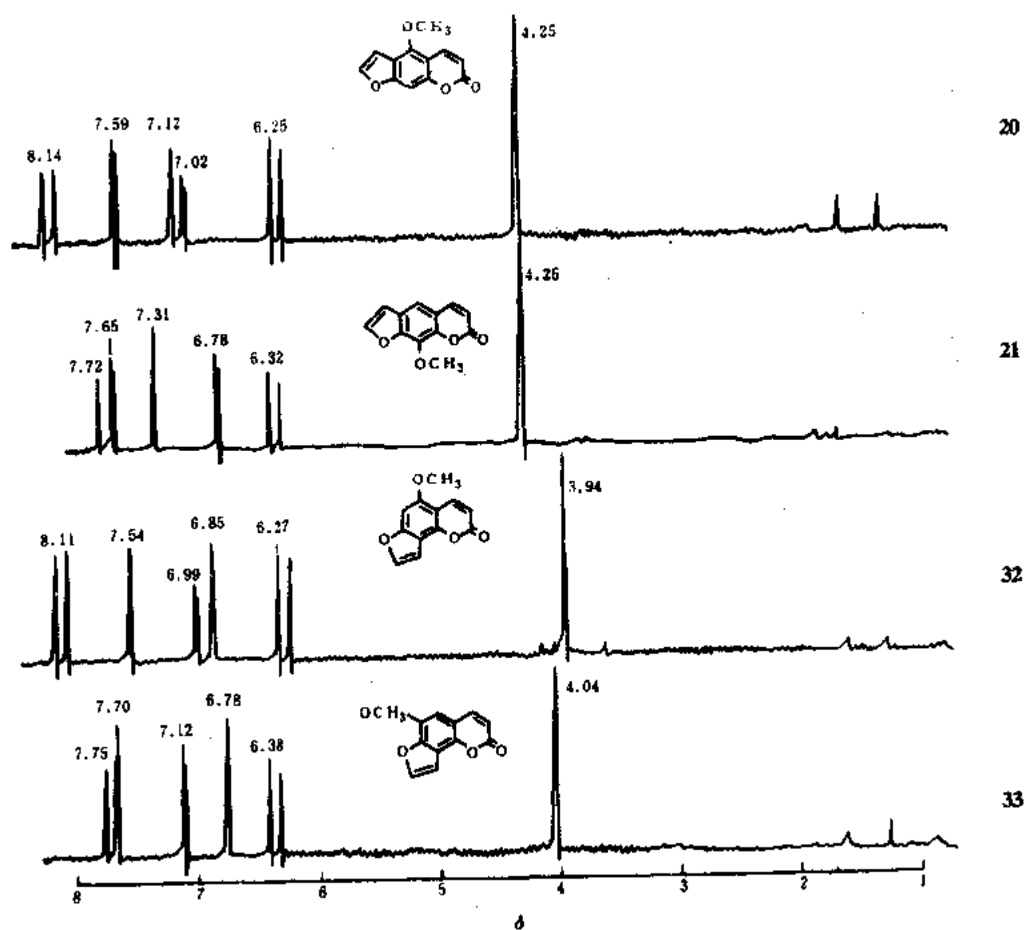


图 10-2 若干不同类型甲氧基呋喃香豆素的^{1}H-NMR图

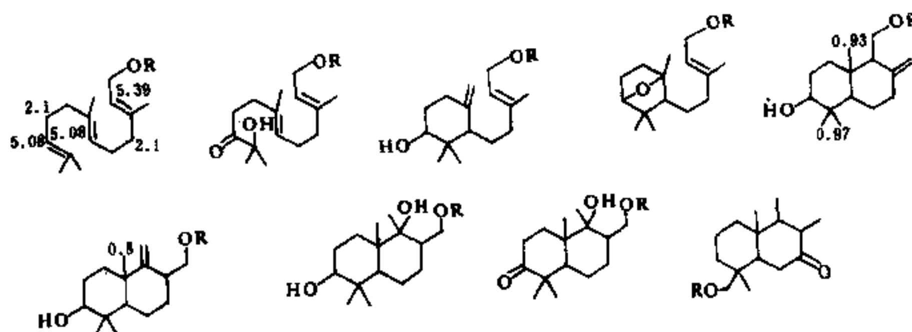
五、二氢呋喃及二氢吡喃香豆素化合物的¹H-NMR 化学位移和偶合常数

表 10-6 二氢呋喃香豆素及二氢吡喃香豆素 52～62 的¹H-NMR 化学位移和偶合常数①

取代基 / 化合物	a-H	b-H	CH_3^-	酯基 H	文献
52	3.20d(8.5)	4.72t(8.5)	1.24,1.36s	—	—
53	3.32d(8.5)	5.04t(8.5)	1.58,1.64s	5.98q(1)q(7)	14
54	3.21d(8.5)	5.13t(8.5)	1.52,1.59s	5.53q(1)	—
55	3.29d(8.5)	4.76t(8.5)	1.24,1.36s	—	—
56	3.36d(8.5)	5.12t(8.5)	1.60,1.65s	5.94q(1)q(7)	
57	3.35d(8.7)	5.21t(8.7)	1.52,1.60s	5.97q(1)	15
58	2.80d(6)d(17)	3.86d(5)d(6)	1.35,1.38s	—	—
	2.07d(5)d(17)				
59	2.83d(5)d(18)	5.07t(5)	1.36,1.38s	5.67q(1)	—
	3.19d(5)d(18)				
60	2.93d(5.5)d(18)	3.89t(5.5)	1.36,1.41s	—	—
	3.15d(5.5)d(18)				
61	2.95d(5)d(18)	5.15t(5)	1.34,1.36s	5.65q(1)	—
	3.22d(5)d(18)				
62	2.6～3.4m	5.0～5.3t	1.33s	2.1～2.4t	16

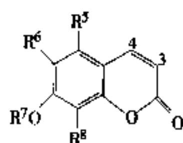
① 表中括号内的数字为偶合常数值。

7-羟基香豆素倍半萜衍生物的¹H-NMR 化学位移如下：

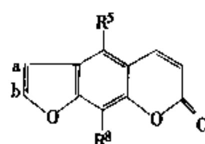


R＝7-香豆素

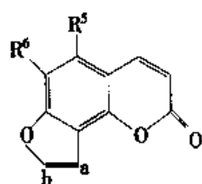
香豆素化合物的结构式如下：



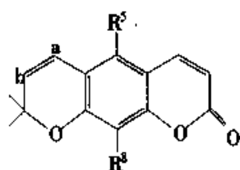
化合物＼取代基	R^5	R^6	R^7	R^8
1	H	H	H	H
2	H	H	CH_3	H
3	H	HO	H	H
4	H	CH_3O	H	H
5	H	CH_3O	CH_3	H
6	H	H	H	HO
7	CH_3O	H	CH_3	H
8	H	H	3-甲基-2-丁烯基	H
9	H	3-甲基-2-丁烯基	H	H
10	H	3-甲基-2-丁烯基	CH_3	H
11	H	H	H	3-甲基-2-丁烯基
12	H	H	CH_3	3-甲基-2-丁烯基
13	H	HO	3-甲基-2-丁烯基	H
14	CH_3O	H	CH_3	3-甲基-2-丁烯基
15	H	H	CH_3	3-甲基-2-丁烯基氧化物
16	H	H	CH_3	3-甲基-2-丁烯基二醇
17	CH_3O	H	CH_3	3-甲基-2-丁烯基氧化物
18	CH_3O	H	CH_3	3-甲基-2-丁烯基二醇



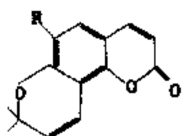
化合物＼取代基	R^5	R^8
19	H	H
20	OCH_3	H
21	H	OCH_3
22	OCH_3	OCH_3
23	*O*-3-甲基-2-丁烯基	Hiso
24	H	*O*-3-甲基-2-丁烯基
25	*O*-3-甲基-2-丁烯基	OCH_3
26	OCH_3	*O*-3-甲基-2-丁烯基
27	*O*-3-甲基-2-丁烯基氧化物	H
28	*O*-3-甲基-2-丁烯基二醇	H
29	H	*O*-3-甲基-2-丁烯基氧化物
30	*O*-3-甲基-2-丁烯基氧化物	OCH_3



取代基 化合物	R^5	R^6
31	H	H
32	OCH_3	H
33	H	OCH_3
34	OCH_3	OCH_3

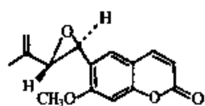


取代基 化合物	R^5	R^8
35	H	H
36	OCH_3	H
37	H	OCH_3

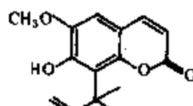


38. R = H

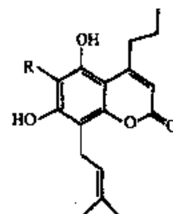
39. R = OCH_3



40

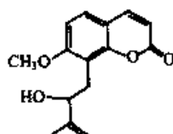


41

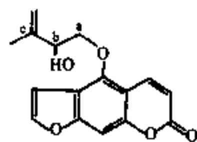


42. R = CO - CH(CH_3)$_2$ CH_2CH_3

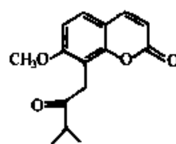
43. R = CO - CH_2CH (CH_3)$_2$



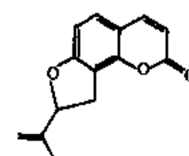
44



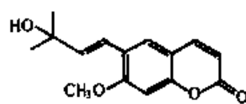
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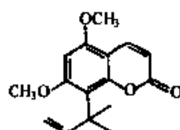
46



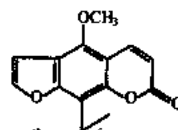
47



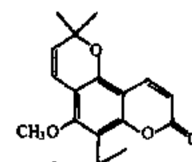
48



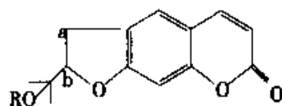
49

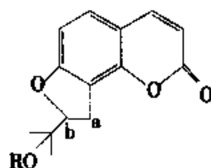


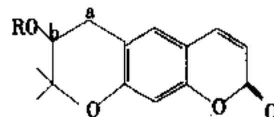
50

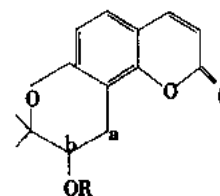


51









52. R = H
53. R = 当归酰基
54. R = 千里光酰基

55. R = H
56. R = 当归酰基
57. R = 千里光酰基

58. R = H
59. R = 千里光酰基

60. R = H
61. R = 当归酰基
62. R = 千里光酰基

表 10-7 羟基可伦比亚甙元衍生物 63～67 的^{1}H-NMR 化学位移

质子 化合物	二氢环 a-H	二氢环 b-H	二氢环 c-CH_3	a-C 酯基 H	c-C 酯基 H	文献
63	5.65	4.91	1.74,1.82	—	5.65m	20
64	6.99	5.55	1.42s	2.20m	—	20
65	6.98	5.24	1.62,1.72s	2.15m	2.15m	—
66	7.12	5.33	1.67,1.74s	6.01q(1)q(7)[c-H]	6.01q(1)q(7)[c-H]	—
67	6.97	5.22	1.66,1.84s	2.05s	5.62q(1.2)	20

表 10-8 顺凯林内酯衍生物 68～76 的^{1}H-NMR 化学位移

质子 化合物	二氢环 a-H	二氢环 b-H	二氢环 c-CH_3	a-C 酯基 H	b-C 酯基 H	文献
68	3.85	5.18	—	—	—	12
69	6.63	5.34	1.43/1.46	6.02q(1)q(7)[c-H]	2.09s[b-3H]	—
70	6.59	5.40	1.41/1.45	2.10s[b-3H]	6.12q(1)q(7)[c-H]	—
71	6.54	5.30	1.41/1.44	2.24m[b-2H]	2.09s[b-3H]	—
72	6.54	5.31	1.40/1.44	2.10s[b-3H]	2.39sext(7)[b-H]	—
73	6.70	5.44	1.46/1.48	6.08q(1)q(7)[c-H]	6.08q(1)q(7)[c-H]	17
74	6.70	5.44	1.46/1.48	5.63q(1)[b-H]	6.08q(1)q(7)[c-H]	18
75	6.58	5.32	1.49	3.03q(5.5)[c-H]	2.12s[b-3H]	19
76	6.67	5.44	1.51	3.05q(5.5)[c-H]	3.05q(5.5)[c-H]	19

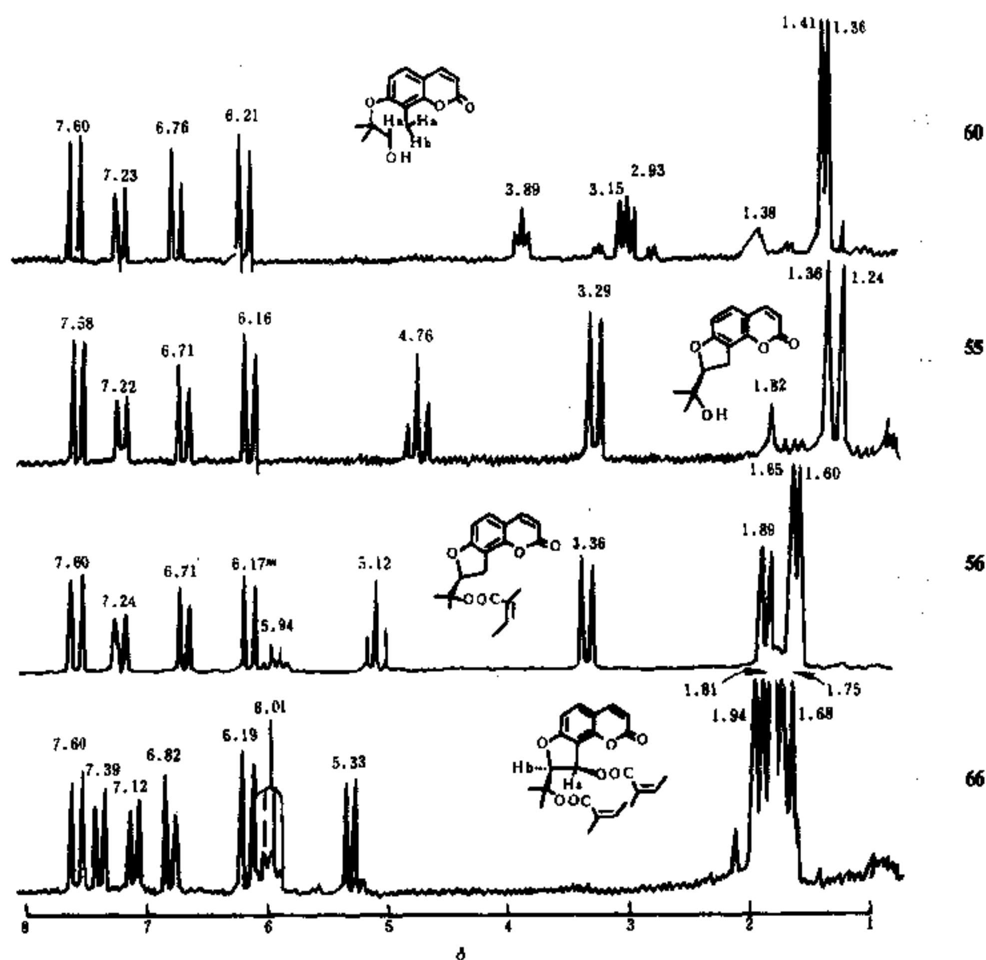


图 10-3 化合物 60、55、56、66 的^{1}H-NMR 谱图

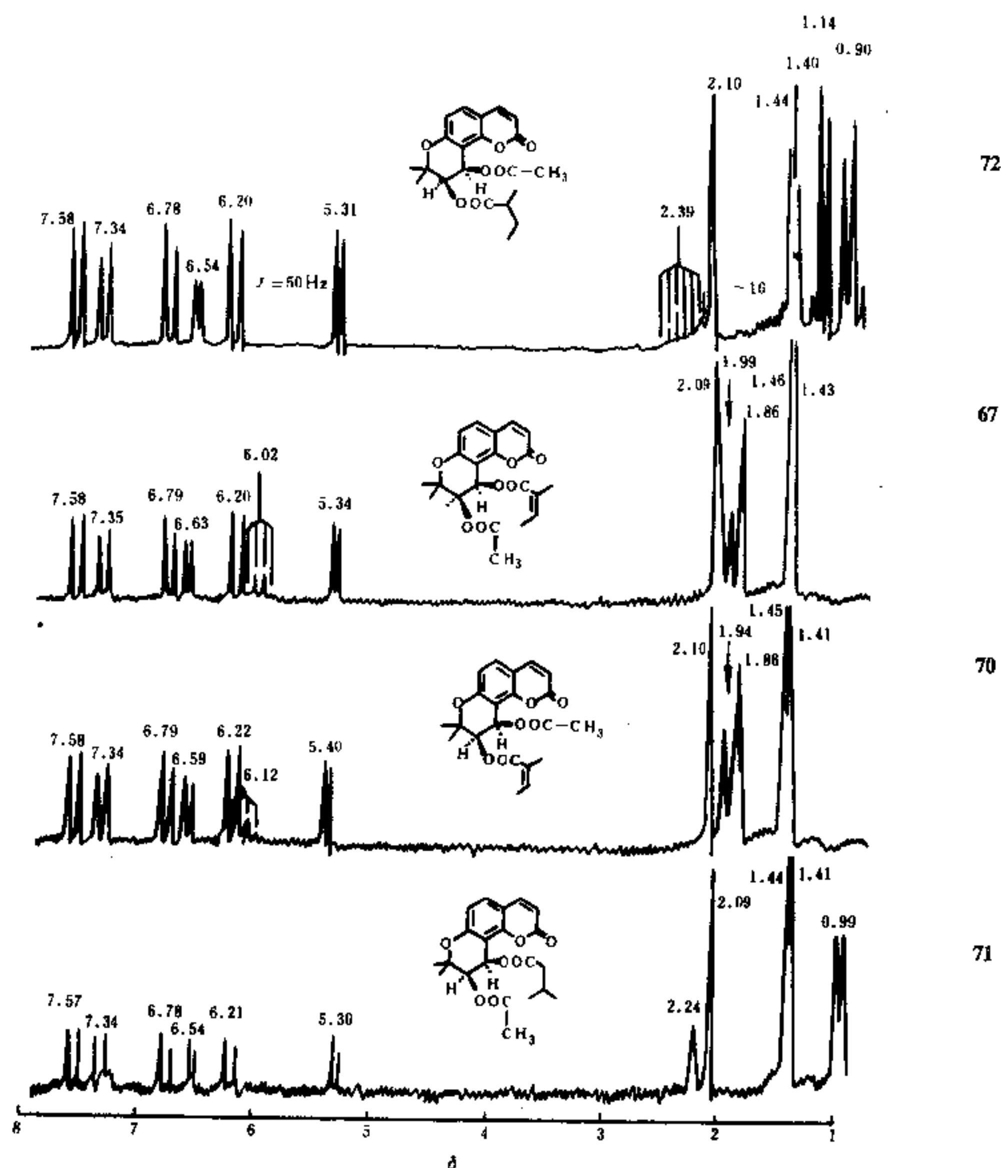
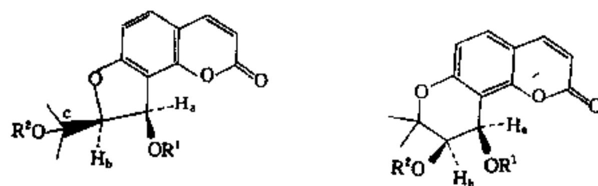


图 10-4 化合物 72、67、70、71 的^{1}H-NMR 谱图



化合物 \ 取代基	R^1	R^2	化合物 \ 取代基	R^1	R^2
63	H	千里光酰基	70	乙酰基	当归酰基
64	异缬草酰基	H	71	异缬草酰基	乙酰基
65	异缬草酰基	异缬草酰基	72	乙酰基	2-甲基丁酰基
66	当归酰基	当归酰基	73	当归酰基	当归酰基
67	乙酰基	千里光酰基	74	千里光酰基	当归酰基
68	H	H	75	2,3-环氧当归酰基	乙酰基
69	当归酰基	乙酰基	76	2,3-环氧当归酰基	2,3-环氧当归酰基

六、3-烯基取代香豆素化合物的^{1}H-NMR化学位移和偶合常数

表 10-9 3-(1,1-二甲烯丙基)取代香豆素 77～83 的^{1}H-NMR 化学位移和偶合常数①

质子 化合物	4-H	5-H	6-H	8-H	a-H	b-H	CH_3—	OCH_3	1,1-CH_3	CH=	=CH_2	文献
77	7.55	7.25	—	7.15	3.4d (7)	≈5t (7)	1.75s	—	1.48[6H]	6.2q(1)	～5	21
78	7.45	6.75s	—	—	3.5d (8)	5	1.62, 1.80	3.85	1.45[6H]	6.3q(d(10)d(16))	4.85～5.2m	22
79	7.50s	6.85s	—	6.81s	—	—	—	3.91 3.93	1.50[6H]	6.18d(10.5)d(18)	5.06d(18)d(1.5) 5.08d(10.5)d(1.5)	—
80	7.55s	7.23d (9)	6.9d (9)	—	—	—	—	4.00	1.56[6H]	6.28qd(10)d(16)	5.12q[d(1.5)]	22
81	7.45s	7.23s	—	6.72s	3.20d (9)	4.75t (9)	1.24, 1.36	—	1.48[6H]	6.20d(10)d(18)	5.05d(18)d(1) 5.08d(10)d(1)	23
82	7.48s	7.19s	—	6.71s	3.19d (7.5)	5.08t (7.5)	1.51, 1.56	—	1.50[6H]	6.18d(10.5)d(18)	5.06d(18)d(1.5) 5.08d(10)d(1.5)	—
83	7.4s	6.9s	—	—	3.47d (7)	4.85～ 5.3m	1.66, 1.85	4.05 —	1.46[6H]	6.20q	5.17q[d(1.5)] 4.85～5.3m	22

① 表中括号内的数字为偶合常数值。

七、多取代呋喃香豆素化合物的^{1}H-NMR化学位移和偶合常数

表 10-10 多取代呋喃香豆素 84～87 的^{1}H-NMR 化学位移和偶合常数①

质子 化合物	5-H	8-H	a-H	b-H	—OCH_3	文献
84	8.04s	7.44d(1)	6.87d(1)d(2.5)	7.73d(2.5)	4.35,3.98	23
85	—	7.25d(1)	6.95d(1)d(2.5)	7.63d(2.5)	4.23,4.05,3.93	24
86	7.68s	—	6.88d(2.5)	7.76d(2.5)	4.37,4.3,3.97	
87	—	6.86d(1)	6.98d(1)d(2.5)	7.55d(2.5)	4.18,3.32	25

① 表中括号内的数字为偶合常数值。

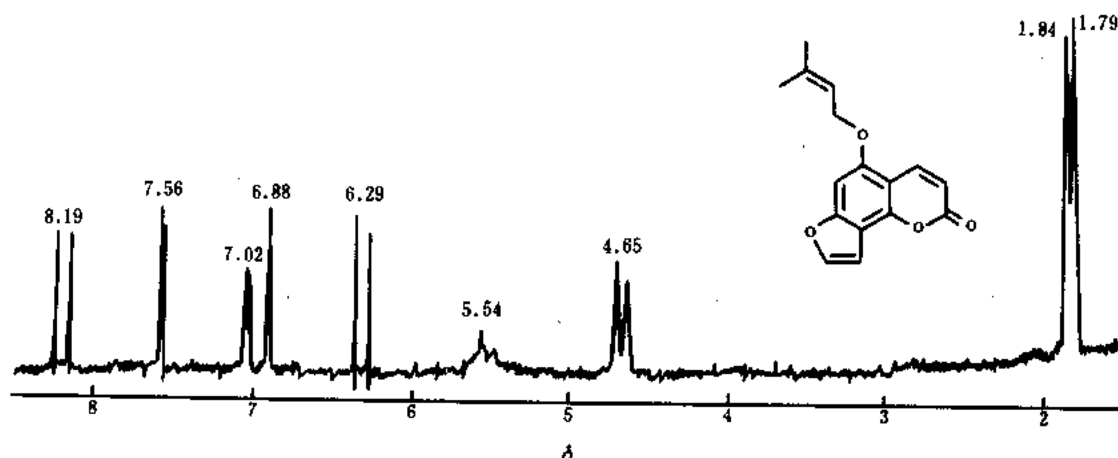
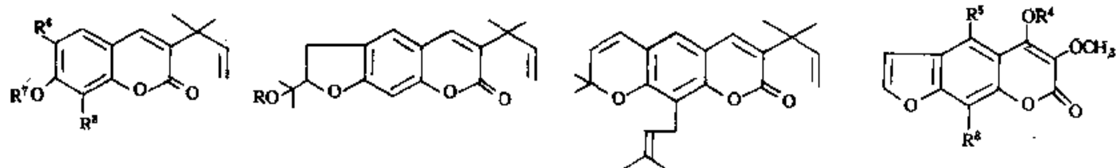


图 10-5 拉拉亭的^{1}H-NMR 谱图



77. R^6 = $OCOCH_3$, R^7 = H, R^8 = H
78. R^6 = $OCOCH_3$, R^7 = H, R^8 = OCH_3
79. R^6 = CH_3O, R^7 = CH_3, R^8 = H
80. R^6 = H, R^7 = CH_3, R^8 = CH_3O

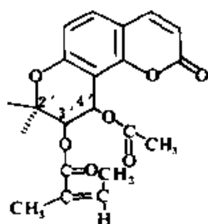
81. R = H
82. R = CH_3CO

83

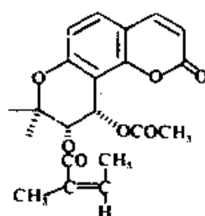
84. R^5 = R^8 = H, R^4 = CH_3
85. R^5 = OCH_3, R^8 = H, R^4 = CH_3
86. R^5 = H, R^8 = OCH_3, R^4 = CH_3
87. R^5 = OCH_3, R = H, R^4 = 1,1-二甲丙烯基

表 10-11 吡喃香豆素 88～95 分子中吡喃环氢的 ^{1}H-NMR 化学位移[26]

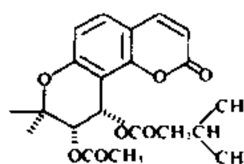
质子＼化合物	88	89	90	91	92	93	94	95
3′-H	5.44d(6)	5.40d(6)	5.34d(4)	3.80d(5.5)	3.73d(6)	5.30d(2.5)	5.26d(3.0)	5.39d(5)
4′-H	6.62d(6)	6.68d(6)	6.58d(4)	5.18d(5.5)	4.90d(6)	4.66d(2.5)	5.05d(3)	6.58d(5)
2′-CH_3	1.47,1.52	1.47,1.49	1.43,1.48	1.40,1.44	1.25,1.44	1.52,1.56	1.36,1.48	1.43,1.45



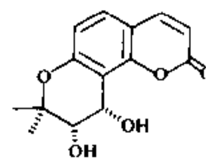
88



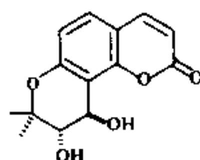
89



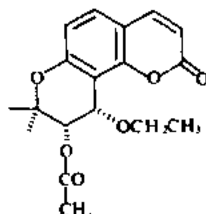
90



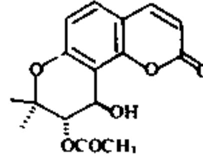
91



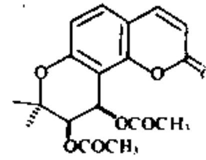
92



93



94

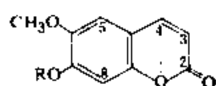


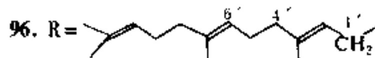
95

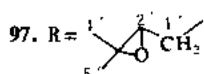
八、不同取代基香豆素化合物的^{1}H-NMR化学位移

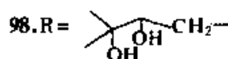
表 10-12 不同取代基香豆素 96～102 的^{1}H-NMR化学位移[27]

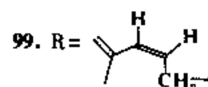
质子＼化合物	96	97	98	99	100	101	102
3-H	6.22d	6.28d	6.32d	6.34d	6.34d	6.23d	6.40d
4-H	7.62d	7.62d	7.63d	7.63d	7.63d	7.60d	7.66d
5-H	6.84d	6.92s	6.87s	6.99s	6.98s	6.93s	6.97s
8-H	6.83d	6.88s	6.86s	6.92s	6.93s	6.85s	7.07s
1'-H	4.70bd	4.35dd	4.32dd	6.31d	6.62d	—	—
2'-H	5.49bt	4.12dd	4.16dd	5.48d	6.27d	—	—
		3.12dd	3.80m	5.12bs	4.97bs	—	—
4'-H	—	1.40s	1.35s	4.95bs	4.93bs	—	—
5'-H	—	1.39s	1.31s	2.08bs	1.91bs	—	—
OCH_3	3.99s	3.92s	3.90s	3.92s	3.93s	3.96s	3.88s

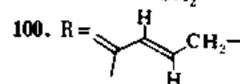




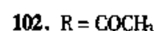










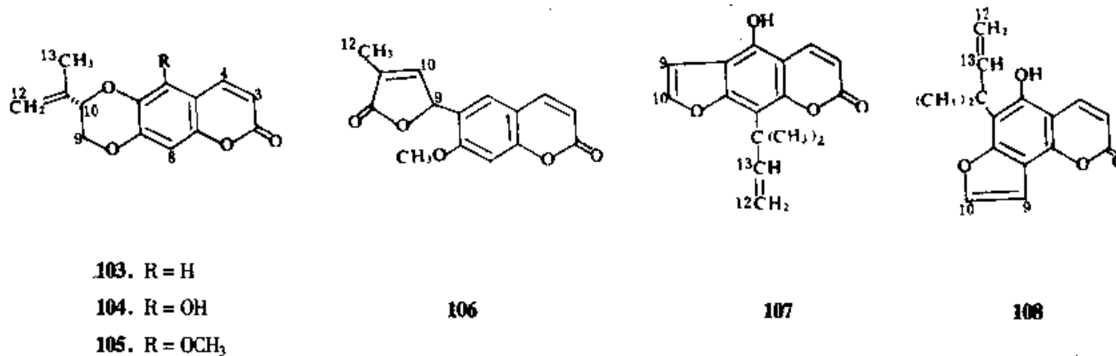


九、其他香豆素化合物的^{1}H-NMR化学位移

表 10-13 香豆素化合物 103～108 的^{1}H-NMR化学位移[28～30]①

质子＼化合物	103	104	105	106	107	108
3-H	6.27d(9.5)	6.22d(9.5)	6.23d(9.5)	6.36d(9.5)	6.18d(9.5)	6.30d(9.5)
4-H	7.57d(9.5)	7.98d(9.5)	7.57d(9.5)	7.76d(9.5)	8.25d(9.5)	8.13d(9.5)
5-H	7.01	—	—	7.46s	—	—
8-H	6.87s	6.47s	6.64s	6.95s	—	—
9-H_A	4.39dd	4.39dd	4.38dd	6.28d	7.22d(2)	7.02d(2)
9-H_B	4.04dd	4.06dd	4.04dd	—	—	—
10-H	4.54bdd	4.57bdd	4.54bdd	7.41m	7.71d(2)	7.56d(2)
12-H_A	5.14bs	5.17bs	5.14bs	1.97bs	4.95d	5.47d
12-H_B	5.19bs	5.20bs	5.21bs	—	4.97d	5.54d
13-H	1.86bs	1.87bs	1.86bs	—	6.37dd	6.44dd
OCH_3	—	—	4.03s	4.04s	—	—

① 表中括号内的数字为 J 值。



103. R = H
104. R = OH
105. R = OCH_3

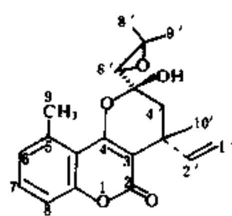
106

107

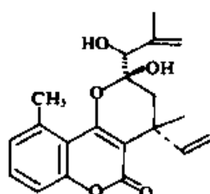
108

表 10-14 香豆素化合物 109 ~ 116 的 ^{1}H-NMR 化学位移[31~33]

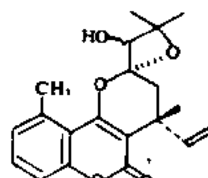
质子 \ 化合物	109	110	111	112	113	114	115	116
6-H	7.02bd	7.01bd	7.02bd	7.04bd	7.15bd	7.33bd	7.26bd	7.19bd
7-H	7.35dd	7.33dd	7.33dd	7.36dd	7.34dd	7.49dd	7.39dd	7.39dd
8-H	7.15bd	7.14bd	7.14bd	7.15bd	7.02bd	7.29bd	7.11bd	7.04bd
9-H	2.74bs	2.75bs	2.80bs	2.75bs	2.70bs	5.59bs	2.87bs	2.68bs
1′-H$_A$	5.10d	5.11m	5.18d	5.07dd	3.45bd	3.44bd	3.11t	3.11t
1′-H$_B$	5.15d	—	5.08d	5.22dd	—	—	—	—
2′-H	6.10dd	6.11dd	6.26dd	6.47dd	5.38bt	5.38bt	4.83t	4.91t
4′-H$_A$	2.23bd	1.89bd	2.39d	5.04s	2.17bs	2.15bs	1.35s	1.41s
4′-H$_B$	2.03d	1.81d	2.04d	—	—	—	—	—
6′-H	3.05s	4.38d	4.57s	4.08d	5.06bt	5.08bt	1.28s	1.31s
8′-H	1.50s	1.86bs	1.53s	1.38s	1.62bs	1.62bs	—	—
9′-H	1.39s	4.50d 5.11m	1.41s	1.32s	1.69bs	1.70bs	—	—
10′-H	1.70s	1.73s	1.61s	1.64s	1.86bs	1.86bs	—	—



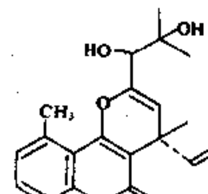
109



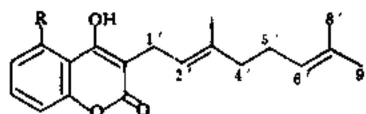
110



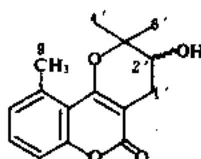
111



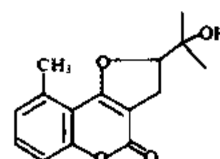
112



113. R = CH_3
114. R = CH_2OCOCH_3



115

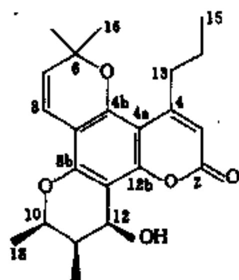


116

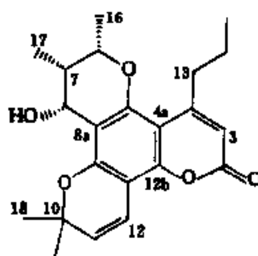
表 10-15 香豆素化合物 117～121 的^{1}H-NMR 化学位移[39]①

质子＼化合物	117	118	119	120	121
3-H	5.94,s	5.94,t,(1.0)	6.02,s	5.98,t,(1.0)	5.79,s
6-H	—	4.32,dq,(2.5,7.0)	—	4.69,dq,(3.0,6.5)	4.22,m
7-H	5.54,d,(10.0)	2.22,ddq,(2.5,6.0,7.0)	5.57,d,(10.0)	2.61,dq,(3.0,7.0)	2.42,m
8-H	6.63,d,(10.0)	5.06,dd,(6.0,1.5)	6.63,d,(10.0)	—	—
10-H	4.39,dq,(6.7,3.3)	—	4.67,dq,(7.0,3.5)	—	—
11-H	2.28,m	5.56,d,(10.5)	2.66,dq,(7.0,3.0)	5.61,d,(11.0)	5.58,d,(10)
12-H	5.09,dd,(6.0,1.0)	6.83,d,(10.5)	—	6.78,d,(11.0)	6.85,d,(10)
13,13′-H	2.29,m 2.86,m	2.88,ddd 2.77,ddd	2.85,dt,(7.0,2.5)	2.85,m	2.81,t
14,14′-H	1.66,m	1.60,sext,(7.0)	1.61,sext,(7.5)	1.63,sext,(7.0)	
15-H	1.04,t,(7.0)	0.98,t,(7.5)	1.00,t,(7.5)	1.01,t,(7.5)	1.00,t
16-H	1.49,s	1.41,d,(7.0)	1.52,s	1.42,d,(7.0)	1.53,d,(7)
17-H	1.49,s	1.06,d,(7.5)	1.51,s	1.14,d,(7.5)	1.15,d,(7)
18-H	1.42,d,(7.0)	1.46,s	1.39,d,(7.0)	1.50,s	1.51,s
19-H	1.14,d,(7.0)	1.46,s	1.13,d,(7.5)	1.50,s	1.51,s
OH	3.29,d,(1.0)	3.64,d,(1.5)	—	—	—

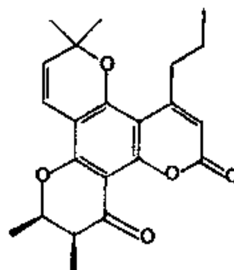
① 括号内数据为偶合常数。



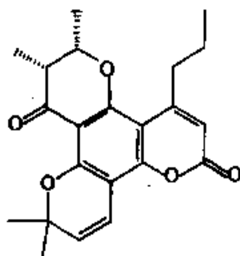
117



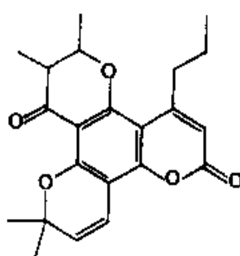
118



119



120



121

十、香豆素化合物的^{1}H-NMR 特征鉴别[38]

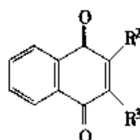
表 10-16 天然香豆素化合物的^{1}H-NMR 系统鉴别表

序 号	化学位移值范围①	结 构 特 征
1-a	δ 6.1~6.4d(9.5) 7.5~7.9d(9.5)	C_5 不含氧取代基的香豆素核
1-b	δ 6.1~6.4d(J≈9.5Hz) 7.9~8.2d(J≈9.5)	C_5 含氧取代基的香豆素核
1-c	δ 6.6~6.9d(8.5) 7.1~7.5d(8.5)	C_8 取代香豆素
1-d	δ<7.0dd(2.5)	C_5,C_7 取代的香豆素(核对 1-b)
1-e	δ 6.7~7.2d(2.5) 7.5~7.7d(2.5)	呋喃香豆素(呋喃环氧邻位的苯环含有取代基)
1-f	δ 7.5~7.7d(2.5) 6.7~7.2dd(2.5;1)	呋喃香豆素(呋喃环氧邻位的苯环不含取代基)
1-g	δ 6.3~6.9d(10.0)	吡喃香豆素(核对 2-a)
1-h	δ 6.5~7.1d(5.0)	林内酯(Khellactone 酯)(核对 2-b)
1-i	δ 6.5~7.1d(6.5)	羟基哥伦布(Columbianetin)酯(核对 2-b)
1-j	δ 7.4~7.6s	可能是 3-烷基香豆素
1-k	δ 5.9~6.2qq(7;1)	当归酸酯(核对 3-g)
1-l	δ 6.1~6.3m	可能是 1,1-二甲烯丙基
2.	δ 2.5~6.0	
2-a	δ 5.3~5.8d(10)	吡喃香豆素(核对 1-g)
2-b	δ 5.1~5.5d(5)或(6.5)	凯林内酯(核对 1-h)
2-c	δ 5.9~6.2qq(7,1)	当归酸酯(核对 3-g)
2-d	δ 5.4~5.8q(1)	千里光酸酯(核对 3-f)
2-e	δ 5.1~5.8qqq(1,7)	异戊烯基(核对 3-b)
2-f	δ 3.3~3.7d(2H)(7) δ 4.5~5.0d(2H)	C-异戊烯基(核对 3-b) O-异戊烯基
2-g	δ 4.7~5.3m(2H)	末端 CH_2
2-h	δ 2.8~4.7m(2H)	异戊烯基环氧或二醇(核对 3-c)
2-i	δ 3.0~3.9 或 5.1~5.5m	如同 2-h,当存在酯基移向低场(核对 3-c)
2-j	δ 3.0~3.4d(2H)(8)	二氢呋喃香豆素(核对 2-k)
2-k	δ 4.6~5.0t(8)	二氢呋喃香豆素(核对 2-j)
2-l	δ 3.8~4.4s	芳香 OCH_3
3.	δ 0.5~2.5	
3-a	δ 2.0~2.2s	乙酸酯基
3-b	δ 1.6~1.9dd(J≈1)	异戊烯基;2 个双峰有时成单峰(核对 2-e,2-f)
3-c	δ 1.2~1.9ss	异戊烯基环氧或二醇;二氢呋喃或二氢吡喃环
3-d	δ<1.2(3H)	饱和碳上的甲基
3-e	δ 1.45~1.65s(6H)	可能是吡喃香豆素或 1,1-二甲基丙烯基(核对 1-f,1-j)
3-f	δ 1.8~2.1dd(J≈1)	千里光酸酯(核对 2-d)
3-g	δ 1.8~2.1m	当归酸酯(核对 2-c)

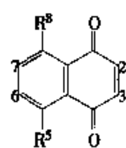
① 括号内数值为 J 值。

第二节　萘醌化合物的^{1}H-NMR 化学位移

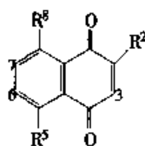
表 10-17　萘醌衍生物的^{1}H-NMR 化学位移



取代基		取代基的化学位移(δ)							
R^2	R^3	H	OH	OCH_3	$OCOCH_3$	$COCH_3$	CH_3	CH_2CH_3	CH_2CH_3
H	H	6.97							
OH	H	6.37							
OCH_3	H	6.17		3.89					
$OCOCH_3$	H	6.76			2.38				
$COCH_3$	H	7.06				2.56			
OH	$COCH_3$					2.77			
						2.85			
CH_2CH_3	H	6.79						2.63	1.21
OH	CH_2CH_3		7.32					2.61	1.11
OCH_3	CH_2CH_3			4.12				2.61	1.10
$OCOCH_3$	CH_2CH_3				2.40			2.56	1.11
OH	OCH_3		6.92	4.23					
$OCOCH_3$	$OCOCH_3$				2.42				
CH_3	H	6.79					2.13		
OH	CH_3		7.35				2.10		
$OCOCH_3$	CH_3				2.42		2.10		



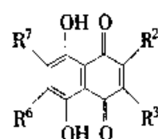
取代基		取代基的化学位移			环上氢的化学位移			
R^5	R^8	H	OCH_3	$OCOCH_3$	C-2	C-3	C-6	C-7
OCH_3	H	7.75	3.99		6.87	6.87	7.28	7.67
$OCOCH_3$	H	8.07		2.46	6.85 或 6.93	6.85 或 6.93	7.39	7.77
OCH_3	OCH_3		3.93		6.75	6.75	7.31	7.31
$OCOCH_3$	$OCOCH_3$			2.45	6.80	6.80	7.40	7.40



取代基			取代基的化学位移①		环氢的化学位移		
R^2	R^5	R^8	OCH_3	$OCOCH_3$	C-3	C-6	C-7
OH	OCH_3	OCH_3	3.95(5) 4.00(8)		6.23	7.40	7.30
$OCOCH_3$	$OCOCH_3$	$OCOCH_3$		2.36(2) 2.48(5,8)	6.62	7.38	7.38

① 括号数字表示取代基的位置。

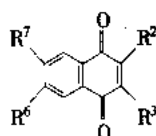
表 10-18 萘茜衍生物的[1]H-NMR 化学位移



取代基			取代基的化学位移①						环氢的化学位移	
R^3	R^6	R^7	H	OH	OMe	Ac	CH_2CH_3	CH_2CH_3	C-5	C-8
Et	H	OMe	6.58		3.96		2.63	1.14	13.33	
Et	OMe	OMe			4.13(6)		2.60	1.13	13.48	12.15
					4.07(7)					
OMe	OMe	Et			4.17(3)					
					4.08(6)					
OMe	Et	OMe			4.20(3)		2.75	1.16		
					4.04(7)					
OMe	Et	OH			4.20		2.68	1.16		
OMe	OH	Et			4.13					
Ac	OMe	OMe		14.28	4.18(6)	2.83			12.75	12.75
					4.07(7)				12.90	12.90
OMe	Ac	OMe			4.20(3)	2.51			12.68	12.00
					4.04(7)					
Ac	OMe	OH			4.24	2.83				
H	OMe	OMe	6.45		4.15(6)					
					4.04(7)					
OMe	OH	H	6.60		4.13					
OMe	H	OH			4.25					

① 括号内数字表示取代基的位置。

表 10-19 胡桃醌衍生物的[1]H-NMR 化学位移



取代基				取代基的化学位移①							
R^2	R^3	R^6	R^7	H	OH	OCH_3	$OCOCH_3$	CH_3CH_3	CH_2CH_3	C-5H	C-8H
H	H	H	H	6.97(2,3)						11.93	7.7
				7.6(7)							
				7.25(6)							
OH	H	H	H	6.28(3)						12.31	
H	OH	H	H	6.33(2)						11.06	
OCH_3	H	H	H	6.09(3)		3.89				12.23	
H	OCH_3	H	H	6.15(2)		3.90				11.70	
H	OCH_3	H	OCH_3	6.08(2)		3.97(3,7)				11.97	7.08
				6.60(6)							
H	CH_2CH_3	H	$OCOCH_3$	6.75(2)			2.32	2.62	1.20	12.16	7.32
				6.99(6)							
OCH_3	OCH_3	H	OCH_3	6.61		3.87(7)				12.09	7.17
						4.07					
						4.11					
OCH_3	OCH_3	H	OH	6.63		4.07				12.04	7.16
						4.11					
OCH_3	OCH_3	CH_2CH_3	OH			4.03		2.72	1.11	12.36	7.13
						4.08					
H	OH	H	OMe	6.72(2)		3.91				11.28	7.08
				6.60(6)							
OMe	Et	H	OH			4.10					

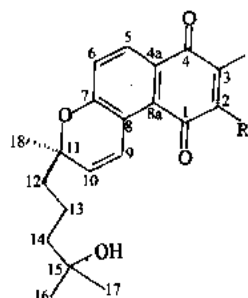
续表

取代基				取代基的化学位移①							
R^2	R^3	R^6	R^7	H	OH	OCH_3	$OCOCH_3$	CH_3CH_3	CH_2CH_3	C-5H	C-8H
OH	H	Et	OMe	6.21(3)		3.98			1.12	12.57	
OMe	H	Et	OH			3.90					
OMe	OH	H	OMe	6.58	6.90	4.15(2) 3.90(7)				11.31	7.23
OMe	OH	Et	OH			4.14					
OH	OMe	Et	OH			4.17					
OH	OH	Et	OMe			3.97					
OMe	OH	Et	OMe			4.14(2) 3.96(7)		2.67	1.11	11.38	7.24
OH	Et	OMe	OMe			4.01(6或7) 3.97(6或7)		2.59	1.13	12.68	7.33
Et	OH	OMe	OMe			4.01(6或7) 3.97(6或7)		2.57	1.11	11.18	7.32
OMe	Et	OMe	OMe			4.12(2) 4.00(6,7)		2.58	1.12	12.48	7.23
Et	OMe	OMe	OMe			4.11(3) 4.01(6或7) 3.99(6或7)			1.13		
OMe	Et	OH	OMe			4.13(2) 4.01(7)					
OH	Et	OH	OMe			4.01			1.12		
OMe	OMe	OMe	OMe			4.08(2,3) 3.98(6或7) 3.97(6或7)					

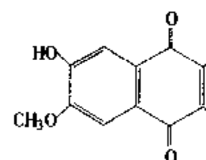
① 括号内数字表示取代基的位置。

表 10-20 萘醌衍生物 122～127 的 ^{1}H-NMR 化学位移[40]

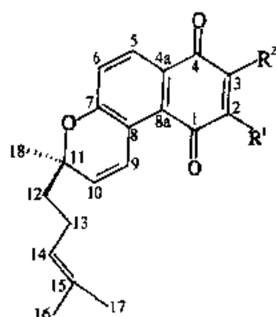
质子＼化合物	122	123	124	125	126	127
5-H	7.95d (8.5)	7.89d (8.5)	7.53s	7.93d (8.5)	7.86d (8.5)	7.99d (8.5)
6-H	7.03dd (8.5,1.0)	6.99dd (8.5,1.0)		7.02d (8.5)	6.96dd (8.5,1.0)	7.11d (8.5)
8-H			7.49s			
9-H	7.81d (10.5)	7.71d (10.5)		7.79d (10.5)	7.69d (10.5)	4.05d (7.0,2H)
10-H	5.92d (10.5)	5.86d (10.5)		5.90d (10.5)	5.83d (10.5)	5.13m
12-H	1.70m, 1.75m	1.64m, 1.74m		1.66m, 1.75m	1.64m, 1.72m	2.05m (2H)
13-H	1.47m	1.50m		2.07m	2.04m	2.05m
14-H	1.44m (2H)	1.43m (2H)		5.04m	5.02m	5.01m
16-CH_3	1.17s	1.16s		1.61s	1.60s	1.63s
17-CH_3	1.18s	1.17s		1.52s	1.51s	1.56s
18-CH_3	1.41s	1.38s		1.41s	1.39s	1.84s
2-CH_3			2.11s			
3-CH_3	2.04s	2.02s	2.11s	2.02s	1.99s	2.04s
2-OCH_3		4.00s			3.97s	
7-OCH_3			4.01s			
OH	4.07s 7.44s	4.07s	6.10s	7.49s		7.49s



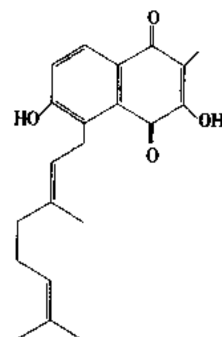
122. R = OH
123. R = OCH_3



124



125. $R^1 = OH, R^2 = CH_3$
126. $R^1 = OCH_3, R^2 = CH_3$

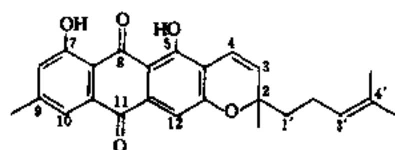


127

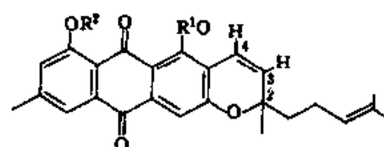
第三节　天然蒽醌类化合物的^{1}H-NMR化学位移

表 10-21　蒽醌衍生物 128～132 的^{1}H-NMR 化学位移[41]

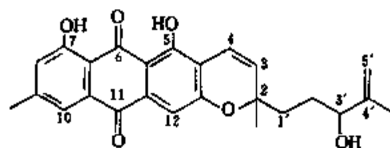
质子＼化合物	128	129	130	131	132a, 132b
3-H	5.69d(10.1)	5.80d(10.1)	5.82d(10.1)	5.68d(10.1)	5.67d(10.0)
4-H	6.80brd (10.1)	6.52brd (10.1)	6.54brd (10.1)	6.80brd (10.1)	6.81brd (10.0)
5-H	12.59s(OH)	2.48s(OAc)	2.49s(OAc)	13.25s(OH)	12.60s(OH)
7-H	12.13s(OH)	2.47s(OAc)	12.76s(OH)	2.45s(OAc)	12.12s(OH)
8-H	7.06d(1.5)	7.98d(1.5)	7.06d(1.5)	8.03d(1.5)	7.06d(1.5)
10-H	7.61d(1.5)	7.17d(1.5)	7.58d(1.5)	7.19d(1.5)	7.61d(1.5)
12-H	7.25bs	7.53bs	7.59bs	7.20bs	7.22bs
3′-H	5.09brt(7.0)	5.07brt(7.0)	5.08brt(7.0)	5.08brt(7.0)	4.32t(6.4) [3.90t(6.4)]
4′-H	1.57bs	1.56bs	1.57bs	1.57bs	1.72bs
5′-H	1.66bs	1.65bs	1.66bs	1.66bs	5.03m



128



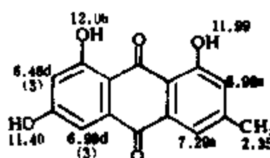
129. $R^1 = R^2 = Ac$
130. $R^1 = Ac, R^2 = H$
131. $R^1 = H, R^2 = Ac$



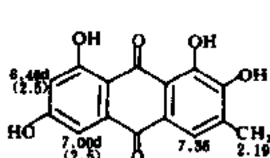
132a. 2(R^*),3'(R^*)

132b. 2(R^*),3'(S^*)

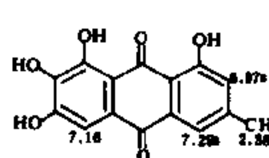
第四节 其他天然蒽醌衍生物 133～146 的^{1}H-NMR 化学位移❶



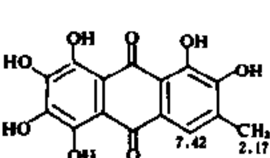
133[34]



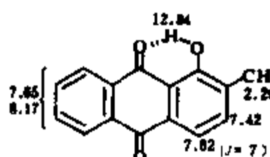
134[34]



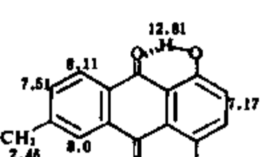
135[34]



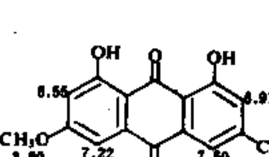
136[34]



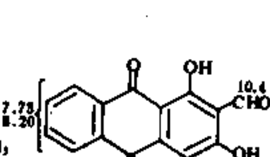
137[35]



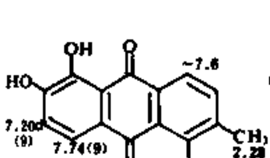
138[35]



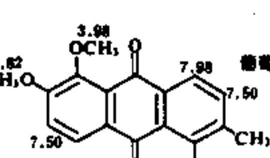
139[35]



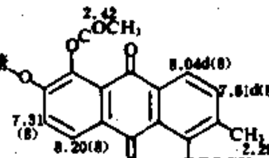
140[35]



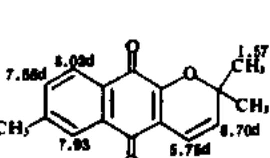
141[36]



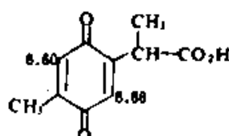
142[36]



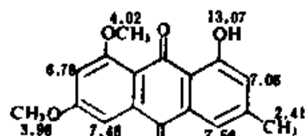
143[36]



144[37]



145[37]



146[37]

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第十一章　其他天然有机化合物的^{1}H-NMR化学位移和偶合常数

第一节　甾体化合物的^{1}H-NMR化学位移

一、雄甾烷衍生物的^{1}H-NMR化学位移

表 11-1　取代基对雄甾烷衍生物 18-CH_3 和 19-CH_3 的^{1}H-NMR化学位移的影响[1~6]

A环取代的5α-甾体	19-CH_3	18-CH_3	A环取代的5α-甾体	19-CH_3	18-CH_3
5α,14α-雄甾烷	0.792	0.692	$\triangle^{3,5}$-7-Oxo	0.367①	0.075①
5α,14β-雄甾烷	0.767	0.992	3α-SH	0.01	0.00
1-Oxo	0.375	0.017	3α-SAc	0.03	0.00
$\triangle^1$	0.050①	0.017①	3α-CN	0.02	0.00
1α-OH	0.017①	0.017①	3α-SCN	0.04	0.00
1β-OH	0.050①	0.008①	3α-NCS	0.02	0.01
$\triangle^1$-3-Oxo	0.250	0.050	3α,4α-环氧	-0.01	0.00
$\triangle^{1,4}$-3-Oxo	0.458	0.100	3α,4α-环硫	0.03	0.00
$\triangle^{1,4,6}$-3-Oxo	0.425	0.150	3β-Et	-0.03	0.00
1α-OAc	0.07	0.00	3β-SH	0.02	-0.01
1β-OAc	0.05	0.00	3β-SH$\triangle^5$	0.00	0.00
1α-,11α-氧桥	0.02	-0.10	3β-SAc	0.02	0.00
2-Oxo	-0.025	0.008	3β-SAc$\triangle^5$	-0.01	0.00
$\triangle^2$	0	0.042①	3β-CN	0.05	0.00
2β-OH	0.250①	0.008①	3β-SCN	0.05	0.01
2β-OAc	0.150①	0	3β-SCN$\triangle^5$	0.04	0.00
2α-Cl	0.083①	0	3β,4β-环硫	0.20	-0.01
2α-Br	0.075①	0	3α-O_2C-Ph	-0.05	0.03
2β-Br	0.233①	0	3β-Br	-0.10	-0.04
2α-OH	0.11	0.00	3β-Cl	-0.10	0.00
2α-Oac	0.13	0.00	3α,4α-CCl_2	0.07	0.00
2α-SH	0.06	0.00	3α,4α-CF_2	0.04	0.00
2α-SAc	0.12	0.00	$\triangle^{1,4}$-3-Oxo	-0.46	-0.05
2β-SH	0.28	0.00	$\triangle^{1,4,6}$-3-Oxo	0.43	-0.13
2β-SAc	0.13	0.00	$\triangle^4$-3-Oxo	-0.41	-0.05
3-Oxo	0.242	0.042	$\triangle^{4,6}$-3-Oxo	-0.33	-0.11
3α-OH	0	0.008	3α-O_2C-PH	-0.05	0.03
3β-OH	0.033	0.008	4-Oxo	-0.033	0.017
3β-OH($\triangle^5$)	0.008	0	$\triangle^4$	0.250	0.042
3α-OAc	0.025	0.017	4β-OH	0.267①	0.008①
3α-OAc($\triangle^4$)	-0.017①	0.008①	4β-OAc	0.225①	0
3β-OAc	0.050	0.008	4α-Br	0.075①	
3β-OAc($\triangle^4$)	0.042	0.008	3α,4α-环氧	-0.01	0.00
3β-OAc($\triangle^5$)	0.017	0	3α,4α-环硫	0.03	0.00
3β-OCH^3	0.025①	0.008①	3β,4β-环硫	0.20	-0.01
3-乙二缩酮($\triangle^5$)	0.025	0.017	4α-SH	0.06	0.00
$\triangle^4$-3-Oxo	0.417	0.075	4α-SAc	0.13	0.01
$\triangle^{3,5}$	0.200①	0.058①	4β-SH	0.24	0.00

续表

A环取代的5α-甾体	$19-CH_3$	$18-CH_3$
4β-SAc	0.08	0.00
4β-SCN	0.07	0.00
3α,4α-CCl_2	0.07	0.00
3α,4α-CF_2	0.04	0.00
4β-Cl	-0.10	0.09
4β-CH_3	-0.07	0.00
4α-CH_3	0.10	0.00
Δ^5	0.233①	0.042①
5α-OH	0.058①	0.008①
5α,6α-氧桥	0.250	
5α-CH_3	0.150	0
5α-Cl	0.250	-0.008
5α-Br	0.317	0
5α-CN	0.125①	0
Δ^5-7-Oxo	0.392	0.042
$\Delta^{5,7}$	0.142①	-0.025①
5α-OAc	0.20	0.00
5α-SH	0.25	0.01
5α-SAc	0.25	-0.02
$\Delta^{5(10)}$		-0.03
5α-,6α-氧桥	-0.14	0.06
5α-CH_3	-0.15	0.00
6-CH_3(Δ^5)	-0.02	-0.01
5β,14α-雄甾烷	0.925	0.692
5β,14β-雄甾烷	0.900	0.992
1-Oxo	0.217①	0
3-Oxo	0.117	0.042
3α-OH	0.008	0.008
3β-OH	0.050	0.008
3α-OAc	0.025	0.008
3β-OAc	0.058	0.008
3β,4β-氧桥	-0.042	0.017
3-乙二缩酮	0.033	
3α-$OCOCH_2CH_2COOCH_3$	0.025	0.017
4-Oxo	0.200	0
4α-OH	0.008①	0.008
5β,6β-氧桥	0.042	
B环和C环取代的5β-甾体	$19-CH_3$	$18-CH_3$
5α,14α-雄甾烷	0.792	0.692
5β,14α-雄甾烷	0.925	0.692
5α,14β-雄甾烷	0.767	0.992
5β,14β-雄甾烷	0.900	0.992
6-Oxo	-0.050	0.017
Δ^6	-0.025	0.050
6α-OH	-0.008①	0.008
6β-OH在5α-甾体	0.225	0.042
6β-OH在5β-及Δ^4-甾体	0.192	0.042
6α-OAc	0.042①	0.008
6β-OAc在5α-甾体	0.183	0.042
6β-OAc在5β-及Δ^1-甾体	0.092	0.050
6α-CH_3	0	0
6β-CH_3	0.075	0
6α-F	0.008①	0
6β-Cl	0.317	0.058

A环取代的5α-甾体	$19-CH_3$	$18-CH_3$
6β-Br	0.250	0.067
6β-SH	0.27	0.06
6β-SCN	0.09	0.04
6β-SAc	0.09	0.03
6-OH,6β-CH_3	-0.18	-0.01
6β-CN	0.283①	0.050
7α-OH,6β-Cl	-0.23	
5α-,6α-氧桥	-0.14	0.06
6β-,19-氧桥		-0.03
6α-Cl	-0.04	0.00
6β-F	-0.13	-0.04
6β-OCH_3	-0.07	0.00
6-CH_3(Δ^5)	-0.02	-0.01
6-=CH_2	0.08	-0.01
6β-C_2H_5	-0.03	
7-Oxo	0.275	0.008
Δ^7	-0.008	-0.117
7α-OH	-0.008	0.008
7β-OH	0.025	0.033
7α-OAc	0.008	0
7β-OAc	0.042	0.042
$\Delta^{7,9}$	0.092①	-0.150
Δ^7及9α,11α-氧桥	0.183	-0.083
7,11-及8α,9α-氧桥	0.408	0.058
7α-OH,6β-Cl	-0.23	
7α-OCH_3		0.00
$\Delta^{8(9)}$	0.125	-0.083
$\Delta^{8(14)}$	-0.117	0.175
8β-OH	0.183	0.183
8α,14α-氧桥	0.075	0.300
8β,14β-氧桥	0.100	-0.033
$\Delta^{8(9)}$-11-Oxo	0.283①	0.033
Δ^8	-0.09	
Δ^8-11-Oxo	-0.29	
8α,9α-氧桥	0.10	
$\Delta^{9(11)}$	0.142	-0.067
9α-OH	0.142	0
9α,11α-氧桥	0.200	0
9β,11β-氧桥	0.117	0.183
9α-F	0.133①	0
9α-Br(11-Oxo)	0.133	0.025
$\Delta^{9(11)}$-12-Oxo	0.267①	0.267
$\Delta^{9(11)}$-11-OH-12-Oxo	0.300①	0.308
Δ^9-12-Oxo	-0.32	
8α-,9-氧桥	0.10	
9β,11β-氧桥 12α-CH_3	-0.27	-0.27
9α-Cl	-0.26	0.01
9α-Br	-0.16	-0.04
10β-OH		(0.04)
10-CO_2H		0.03
10-CHO		0.04
11-Oxo	0.217	-0.033
Δ^{11}	-0.033	0.083
11α-OH	0.117	0.025

续表

A环取代的5α-甾体	19-CH_3	18-CH_3	A环取代的5α-甾体	19-CH_3	18-CH_3
11β-OH	0.258	0.242	15β-OH	0.033[①]	0.267
11α-OAc	0.092	0.058	15α-OAc	0	0.067
11β-OAc	0.067	0.117	15β-OAc	0.042[①]	0.225
11α,12α-氧桥	0.067	0.133	14α-,15α-氧桥	0.025	0.183
11β,12β-氧桥	0.175	0.125	△16-17-$COCH_3$	0.017	0.175
11α-Br(12-Oxo)	0.167[①]	0.008	16β-OAc 及 17α-OH 及 17β-$COCH_3$	0.008[①]	0.242
11β-Br(12-Oxo)	0.367[①]	0.317			
11β-OH,12α-CH_3	-0.27	-0.35	16β-OAc 及 17α-OH 及 17β-$COCH_2OAc$	0.008[①]	0.167
11β-OH,12α-F	-0.27	-0.20			
11-Oxo,12α-OH	-0.23	0.04	16α,17α-氧桥	0.008	0.417
11α-OH,12-Oxo	-0.23	-0.37	16α-CH_3	-0.008	0.008
11α-OAc,12-Oxo	-0.18	-0.40	16α-CH_3 及 17α-OH 及 17β-$COCH_2OAc$	-0.017	0.033
11-Oxo,12α-OAc	-0.28	-0.03			
△8-11-Oxo	-0.29		16α-OH	0.01	0.06
1α-,11α-氧桥	0.02	-0.10	△16	0.01	0.10
9α-,11α-氧桥	-0.200		16α,17α-二OH	0.01	-0.03
9β,11β-氧桥	0.117	0	16α-OAc	0.00	-0.04
9β,11β-氧化物,12α-CH_3	-0.27	-0.27	16β-OAc	-0.02	
11α-Br	-0.18		16α,17α-氧桥	-0.01	-0.45
11β-Br	-0.38		16β-Br	-0.12	-0.47
12-Oxo	0.100	0.375	17-Oxo	0.017	0.167
12-Oxo 及 17β-$COCH_3$	0.092[①]	0.250	17α-OH 及 17β-$COCH_3$	-0.008	-0.008
12-Oxo 及 17β-$COOCH_3$	0.092	0.417	17α-OH 及 17β-$COCH_2OAc$	-0.008	-0.042
12α-OH	-0.008	0.042	17α-OH 及 17β-$COOCH_3$	-0.008[①]	-0.017
12α-OH 及 17β-$COOCH_3$	-0.017	-0.042	17β-OH	0	0.033
12β-OH	0.008	0.067	17β-OH 及 17α-CH_3	0.008	0.150
12α-OAc	-0.025	0.083	17β-OAc	0	0.083
12β-OAc	0	0	17β-OAc 及 17α-CH_3	0.008	0.133
12α-Br(11-Oxo)	-0.025	0.183	17β-C_2H_5	-0.008	-0.142
11β-OH,12α-CH_3	-0.27	-0.35	17β-C_8H_{17}	-0.017	-0.050
11β-OH,12α-F	-0.27	-0.20	17β-C_9H_{19}	-0.017[①]	-0.033
11-Oxo,12α-OH	-0.23	0.04	17β-C_9H_{17}	-0.008	-0.033
11α-OH,12-Oxo	-0.23	-0.37	17β-C_4H_8COOH	-0.008	-0.042
11α-OAc,12-Oxo	-0.18	-0.40	17β-$C_4H_8COOCH_3$	-0.008	-0.050
11-Oxo,12α-OAc	-0.28	-0.03	17β-$C_4H_8COOC_2H_5$	-0.008[①]	-0.050
△9-12-Oxo	-0.32		17β-CH[OH(α)]CH_3	-0.008[①]	-0.050
11α-,12α-氧桥	-0.07		17β-CH[OH(β)]CH_3	-0.008	0.042
11β,12β-氧桥	0.175	0.125	17β-CH[OAc(α)]CH_3	-0.008[①]	-0.033
9β,11β-氧桥 12α-CH_3	-0.27	-0.27	17β-CH[OAc(β)]CH_3	-0.008	-0.083
12α-CH_2O-12β 氧桥	-0.03	-0.27	17β-CH(CH_3)$COOCH_3$	-0.008[①]	-0.033
12α-Br	0.02	-0.22	17β-$COCH_3$	-0.008	-0.083
12α-CH_3	-0.03	-0.11	17β-$COCH_2OH$	-0.008[①]	-0.058
12=CH_2	-0.04	-0.30	17β-$COCH_2OAc$	-0.008[①]	-0.042
12=CHBr	-0.07	-0.37	17β-COOH	-0.008[①]	0.025
12α-CH_2Br	-0.01	-0.33	17β-C(OCH_2)$_2CH_3$	-0.008	0.050
12α-CH_2Cl	-0.05	-0.34	17β-C(=$NNHCONH_2$)CH_3	0	-0.133[①]
D环取代的 14α-甾体	19-CH_3	18-CH_3	17α-$COOCH_3$	-0.017[①]	0.158
5α,14α-雄甾烷	0.792	0.692	17β-$COOCH_3$	-0.008	-0.050
5β,14α-雄甾烷	0.925	0.692	17β-$OCOC_2H_5$	0	0.083
△14	0.008	0.250	17β-$OCOC_6H_5$	0	0.225[①]
14α-OH	0	0.117	17β-$OCOC_6H_{11}$	-0.008[①]	0.083
14α,15α-氧桥	0.025	0.183	17β-$C_4H_5O_2$	0	-0.017
15-Oxo	0.008[①]	0.075	17β-$C_4H_3O_2$	0	-0.067[①]
15α-OH	0.008	0.033	17[=(OAc)CH_3]	0	0.100

续表

A环取代的5α-甾体	19-CH_3	18-CH_3	A环取代的5α-甾体	19-CH_3	18-CH_3
17α-OH	0.01	-0.05	17α-OAc	-0.01	-0.01
17α-Me及17β-OH	0.00	0.15	16α,17α-氧桥	-0.01	-0.45
17α-$O_2CC_5H_{11}$	-0.01	0.03	17α-OCH_3		-0.10
17α-$O_2CC_6H_{13}$	-0.01	-0.01	17α-$COCH_3$	-0.01	-0.20
D环取代基的14β-甾体	**19-CH_3**	**18-CH_3**	**D环取代基的14β-甾体**	**19-CH_3**	**18-CH_3**
5α,14β-雄甾烷	0.767	0.992	14β,15β-氧桥	0.050	0.150
5β,14β-雄甾烷	0.900	0.992	17-Oxo	0.017	0.083
14β-OH	0.017	-0.025	17β-OH	0.008①	0.025
14β-OH及17β-COOH	0.025①	0.108	17α-$COOCH_3$	-0.008	0.158
14β-OH及17β-$COOCH_3$	0.025	-0.017	17β-$COOCH_3$	-0.008	0.067
14β-OH及15-Oxo&17β-$COOCH_3$	-0.017	0.067	17β-$C_4H_5O_2$	-0.017①	-0.025
			17β-$C_4H_3O_2$	-0.008①	-0.100

① 表示仅一个化合物的化学位移值。

表 11-2　D-高-5α-雄甾烷衍生物的^{1}H-NMR化学位移[7,8]

化合物 \ 质子	18-CH_3	19-CH_3	化合物 \ 质子	18-CH_3	19-CH_3
D-高-5α-雄甾烷	0.81	0.77	16α-OH	0.80	0.77
酮类			△^{17}-,16α-OH	0.80	0.80
17a-酮	1.066	0.88	乙酸酯类		
17-酮	0.77	0.77	17aβ-OAc	0.866	0.77
16-酮	1.025	0.79	17aα-OAc	0.90	0.78
醇类			17β-OAc	1.115	0.79
17aβ-OH	0.775	0.775	17α-OAc	0.88	0.76
17aα-OH	0.825	0.78	16β-OAc	0.85	0.77
17β-OH	1.04	0.78	16α-OAc	0.83	0.78
17α-OH	0.82	0.77	△^{17}-,16α-OAc	0.84	0.80
16β-OH	0.84	0.78			

二、胆甾烷衍生物的^{1}H-NMR化学位移

表 11-3　胆甾烷衍生物的部分质子^{1}H-NMR化学位移数据[9~11]

化合物 \ 质子	19-H	18-H	2-H	3-H	4-H	OAc	SAc	其他H
5α-胆甾烷	0.77	0.65						
3β-羟基胆甾-1-烯	0.91	0.66						
胆甾-1-烯-3-酮	1.01	0.76						
3β-乙酰氧基胆甾-1-烯	0.93	0.67						
2β-巯基	1.05	0.65	3.59					
2β-乙酰硫基	0.90	0.65	4.05				2.29	
2β-羟基-3α-巯基	1.00	0.65	3.97	3.24				
2β-羟基-3β-巯基	0.98	0.64	3.83	2.98				
2β-羟基-3α-硫氰酸基	1.02	0.65	4.19	3.75				
2β-乙酰氧基-3α-乙酰硫	0.92	0.64	4.95	3.87		2.05	2.32	
2β-乙酰氧基-3β-乙酰硫基	0.90	0.63	5.11	3.78		2.03	2.28	
2β-乙酰氧基-3α-硫氰酸基	0.94	0.65	5.12	3.82		2.05		
2α-巯基-3β-羟基	0.86	0.64	2.71	3.21				

续表

化合物 \ 质子	19-H	18-H	2-H	3-H	4-H	OAc	SAc	其他 H
2β-巯基-3α-羟基	0.97	0.65	3.23	3.87				
2β-巯基-3α,17β-二羟基-17α-甲基	1.00	0.84	3.24	3.87				17—CH_3 2.20
2β,3α-二巯基	1.02	0.65	~3.42	~3.42				
2α-乙酰硫-3β-乙酰氧基	0.94	0.65	3.72	4.69		2.00	2.29	
2β-乙酰硫-3α-乙酰氧基	0.87	0.63	3.89	4.83		2.08	2.31	
3β,3α-二乙酰硫基	0.91	0.64	~3.94	~3.94			2.32	
2β-硫氰酸基-3α-羟基	0.85	0.66	3.75	4.19				
2β-硫氰酸基-3α-乙酰氧	0.89	0.65	3.81	5.15		2.09		
2α,5-环硫醚	0.92	0.64	3.61					$H_{1\alpha}$ 1.85 $H_{1\beta}$ 1.31
2α,5-顺-环亚砜	2.3	1.0	3.43					$H_{1\alpha}$ 1.78 $H_{1\beta}$ 1.29
2α,5-反-环亚砜	1.10	0.67	3.28					$H_{1\alpha}$ 2.84 $H_{1\beta}$ 1.79
2α,5-环砜	1.00	0.67	2.92					$H_{1\alpha}$ 2.13 $H_{1\beta}$ 1.44
2α,5-氧桥	0.94	0.64	4.37					$H_{1\alpha}$ 1.21 $H_{1\beta}$ 1.29
5-羟基胆甾-2-烯	0.88	0.67						
2α,5-环硫醚-3α-外-羟基	0.85	0.65	3.45	3.93	1.26(α) 2.53(β)			$H_{1\alpha}$ 1.87 $H_{1\beta}$ 1.18
2α,5-环亚砜-3α-外-羟基	0.95	0.65	3.63	1.26	2.21(α) 2.60(β)			$H_{1\alpha}$ 1.76 $H_{1\beta}$ 1.07
2α,5-环硫化物-3α-乙酰氧基	0.89	0.65	3.57	4.87	1.60(α) 2.55(β)			$H_{1\alpha}$ 1.87 $H_{1\beta}$ 1.30
2α,5-环亚砜-3α-乙酰氧基	0.97	0.64	3.66	5.09	2.49(α) 2.49(β)			$H_{1\alpha}$ 1.78 $H_{1\beta}$ 1.28
2α,5-环硫醚-3β-内-羟基	1.05	0.65	3.37	4.53	2.03(α) 2.02(β)			$H_{1\alpha}$ 1.71 $H_{1\beta}$ 2.04
3α,5-环亚砜-3β-内-羟基	1.13	0.65	3.48	4.85	2.39(α) 1.93(β)			$H_{1\alpha}$ 1.55 $H_{1\beta}$ 2.01
2α,5-环硫醚-3β-乙酰氧基	1.02	0.66	3.65	5.18	2.13(α) 1.98(β)			$H_{1\alpha}$ 1.77 $H_{1\beta}$ 1.82
2α,5-环亚砜-3β-乙酰氧基	1.09	0.65	3.75	5.55	2.57(α) 2.01(β)			$H_{1\alpha}$ 1.63 $H_{1\beta}$ 1.72
2α,5-环硫醚-3β-内-溴	1.06	0.66	3.61	4.61	2.27(α) 2.27(β)			$H_{1\alpha}$ 1.82 $H_{1\beta}$ 2.20
2α,5-环硫醚-3β-内-溴	1.14	0.65	3.57	4.89	2.65(α) 2.27(β)			$H_{1\alpha}$ 1.73 $H_{1\beta}$ 2.06
2α,5-环硫醚-3-酮	0.99	0.66	3.60		2.42(α) 2.64(β)			$H_{1\alpha}$ 2.13 $H_{1\beta}$ 1.63
2α,5-表亚砜-3-酮	1.07	0.66	3.83		2.78(α) 2.58(β)			$H_{1\alpha}$ 2.09 $H_{1\beta}$ 1.56
3β-乙基	0.74	0.65						
3α-羟基	0.78	0.66		4.05				
3β-羟基	0.80	0.64		3.59				
3α-乙酰氧基	0.79	0.66		5.03		2.06		
3β-乙酰氧基	0.82	0.65		4.70		2.02		
3α-巯基	0.88	0.65		3.52				
3α-乙酰硫基	0.80	0.65		3.00			2.30	
3α-氰基	0.79	0.65		2.95				
3β-氰基	0.82	0.65		2.34				
3α,4α-氧桥	0.76	0.65		3.13	2.67			

续表

化合物 \ 质子	19-H	18-H	2-H	3-H	4-H	OAc	SAc	其他 H
3α,4α-环硫醚	0.80	0.65		3.20	2.58			
3β,4β-环硫醚	0.97	0.64						
3α-羟基-4α-巯基	0.83	0.65		3.78	3.05			
3α-羟基-4β-巯基	0.97	0.64		3.95	3.09			
3α-羟基-4β-硫氰酸基	0.81	0.64		4.21	3.50			
3β-羟基-4α-巯基	0.84	0.65		3.18	2.55			
3β,5α-二羟基	0.98	0.66		4.05				
3β-羟基-5α-巯基	1.05	0.65		4.33				
3β-羟基-5α-氰基	0.95	0.66		4.12				
3β-羟基-5α,6α-氧桥	1.06	0.63		3.83				
3β-羟基-5β,6β-环硫醚	1.15	0.64		3.81				
3β,6β-二羟基	1.04	0.70						
3β-羟基-6-酮	0.75	0.67		3.53				
3β-羟基-6β-巯基	1.05	0.71		3.64				
3α-乙酰氧基-4α-乙酰硫基	0.93	0.65		5.05	3.76	2.05	2.27	
3α-乙酰氧基-4β-乙酰硫基	0.85	0.65		4.83	3.73	2.07	2.30	
3α-乙酰氧基-4β-硫氰酸基	0.84	0.65		5.20	3.59	2.09		
3β-乙酰氧基-4α-乙酰硫基	0.94	0.65		4.70	3.62	1.98	2.30	
3β-乙酰氧基-5α-羟基	1.00	0.66		5.15		2.01		
3β-乙酰氧基-5α-巯基	1.06	0.65		5.46		2.02		
3β-乙酰氧基-5α-乙酰硫基	1.07	0.63		5.30		2.00	2.27	
3β-乙酰氧基-5α-氯	1.10	0.66		5.33				
3β-乙酰氧基-5β,6β-氧桥	1.02	0.65		4.75		2.03		
3β-乙酰氧基-5α,6α-硫醚	1.20	0.61		4.94		2.00		
3β,6β-二乙酰氧基	1.02	1.70						
3β-乙酰氧基-6-酮	0.77	0.67		4.68		2.01		
3β-乙酰氧基-6β-乙酰硫基	0.91	0.68		4.73		2.00	2.30	
3α-硫氰酸基-4β-羟基	1.04	0.65		3.80	3.80			
3α-硫氰酸基-4β-乙酰氧基	1.02	0.65		3.82	4.93	2.06		
3β,5α,6β-三羟基	1.19	0.69		4.05				
3β,5α-二羟基-6β-巯基	1.26	0.71		4.03				
3β,5α-二羟基-6β-硫氰酸基	1.08	0.70		4.03				
3β,6β-二乙酰氧基-5α-羟基	1.16	0.69		5.14		2.01		
						2.06		
3β-乙酰氧基-5α-羟基-6-酮	0.82	0.65		5.10		2.00		
3β-乙酰氧基-6β-乙酰硫-5α-羟基	1.08	0.68		5.15		2.02		
3β-乙酰氧基-5α-羟基-6β-硫氰酸基	1.08	0.70		5.15		2.05		
3β,5α-二乙酰氧基-6β-乙酰硫	1.11	0.68		4.75		1.98	2.31	
						2.09		
3β-乙酰氧基-6β-羟基-5α-硫氰酸基	1.39	0.70		5.33		2.05		
3β-乙酰氧基-5α-溴-6β-羟基	1.33	0.70		5.42		2.04		
3-酮	1.01	0.68						
3β-羟基胆甾-4-烯	1.53	0.69						
3-酮胆甾-4-烯	1.19	0.72						
3β-乙酰氧基胆甾-4-烯	1.63	0.68						
3β-羟基胆甾-5-烯	1.01	0.67						
3-酮-胆甾-5-烯	1.18	0.72						
3β-乙酰氧基胆甾-5-烯	1.03	0.68						
3-巯基	0.86	0.66						
3β-羟基胆甾-6-烯	0.79	0.69						
3-酮胆甾-6-烯	0.98	0.73						
3β-乙酰氧基胆甾-6-烯	0.80	0.69						
3β-羟基胆甾-7-烯	0.80	0.54						

续表

化合物 \ 质子	19-H	18-H	2-H	3-H	4-H	OAc	SAc	其他H
3-酮胆甾-7-烯	1.02	0.56						
3β-乙酰氧基胆甾-7-烯	0.82	0.54						
3β-羟基-6-甲烯基	0.69	0.65						
3-酮-6-甲烯基	0.90	0.68						
3β-羟基-7-甲烯基	0.94	0.69						
3-酮-7-甲烯基	1.12	0.71						
3β-乙酰氧基-7-甲烯	0.95	0.61						
3-酮胆甾-8-烯	1.14	0.64						
3β-乙酰氧基胆甾-8-烯	0.97	0.61						
3β-羟基胆甾-8(14)-烯	0.70	0.86						
3-酮胆甾-8(14)-烯	0.91	0.88						
3β-乙酰氧基胆甾-8(14)-烯	0.71	0.86						
4β-乙酰硫基	0.84	0.65			3.8		2.25	
4β-巯基-5α-羟基	1.19	0.65			3.08			
4β-乙酰硫基-5α-羟基	1.03	0.65			3.67		2.32	
4β-硫氰酸基-5α-羟基	1.02	0.65			3.48			
Δ^4	1.08	0.68						
Δ^5	1.00	0.68						6-H 5.25
3β-羟基胆甾-5-烯	1.02	0.68		3.50				6-H 5.34
3β-乙酰氧基胆甾-5-烯	1.02	0.68		4.59		2.02		6-H 5.34
3β-巯基胆甾-5-烯	1.00	0.67		2.58				6-H 5.30
3β-乙酰硫基胆甾-5-烯	0.98	0.67		3.30			2.27	6H 5.34
3β-硫氰酸基胆甾-5-烯	1.04	0.68		3.03				6H 5.40
胆甾-3,5-二烯-7-酮	1.10	0.70		6.15	6.08			6H 5.58
胆甾-7-烯	0.77	0.54						
胆甾-8(14)-烯	0.66	0.86						

三、甾体皂甙元化合物的^{1}H-NMR化学位移

表 11-4 甾体皂甙元化合物的部分质子^{1}H-NMR化学位移数据

化合物 \ 质子	19-H	18-H	21-H	27-H	化合物 \ 质子	19-H	18-H	21-H	27-H
1	0.79	0.77	0.96	0.79	**20**	1.30	0.80	0.98	0.78
2	0.77	0.77	0.95	0.79	**21**	1.23	0.74	0.95	0.79
3	0.77	0.77	0.96	0.80	**22**	1.01	0.71	0.94	0.80
4	1.02	0.78	0.96	0.78	**23**	1.08	0.80	0.97	0.78
5	0.80	0.77	0.97	0.80	**24**	1.03	0.79	0.97	0.78
6	0.83	0.78	0.96	0.78	**25**	-1.03	0.80	0.97	—
7	0.82	0.75	—	—	**26**	1.03	0.80	0.98	
8	0.80	0.77	0.96	0.79	**27**	0.78	0.78	0.98	0.78
9	0.83	0.77	0.96	0.78	**28**	0.83	0.76	0.97	0.78
10	0.82	0.75	1.09	0.98	**29**	1.05	0.80	0.97	0.78
11	0.89	0.75	0.95	0.78	**30**	0.95	0.71	0.96	0.79
12	0.99	0.73	0.95	0.79	**31**	1.06	0.72	0.95	0.79
13	0.90	0.78	0.95	0.78	**32**	1.06	1.00	0.95	0.78
14	0.87	0.77	0.96	0.79	**33**	0.93	0.82	0.95	0.78
15	0.87	0.77	1.10	0.98	**34**	0.91	1.05	1.04	0.78
16	0.93	0.76	0.95	0.78	**35**	0.81	0.83	0.98	0.79
17	0.93	0.76	1.10	0.97	**36**	0.82	0.75	1.00	0.79
18	0.92	0.77	0.96	0.79	**37**	0.05	1.01	0.97	0.79
19	1.20	0.83	0.98	0.78	**38**	1.07	0.79	0.96	0.78

续表

化合物 \ 质子	19-H	18-H	21-H	27-H
39	1.03	0.79	0.97	0.78
40	1.04	0.79	0.97	—
41	0.97	0.70	0.96	0.79
42	1.05	0.92	0.95	0.79
43	1.05	0.82	0.92	0.80
44	1.05	0.75	1.17	0.83
45	1.08	1.00	0.96	0.78
46	0.92	1.04	1.06	0.79
47	0.92	1.05	1.00	0.90
48	0.84	0.84	0.92	0.78
49	0.86	0.86	1.08	0.78
50	1.25	0.85	0.97	0.79
51	1.17	0.78	0.96	0.78
52	1.04	0.72	0.95	0.79
53	0.95	1.05	1.06	0.79
54	1.00	1.03	1.05	0.79
55	1.13	0.88	0.98	0.81
56	1.20	0.83	0.97	0.79
57	1.20	0.83	0.98	0.79
58	1.00	0.77	—	—
59	1.11	1.09	1.06	0.78
60	1.02	0.83	0.97	0.78
61	1.03	0.83	0.90	0.79
62	1.08	0.93	1.10	0.79
63	1.02	0.78	0.98	0.79
64	1.42	1.11	0.95	0.79
65	1.09	0.93	1.10	0.79
66	1.46	0.81	0.96	0.79
67	1.30	0.83	0.98	—
68	1.34	0.83	0.97	0.78
69	1.42	0.81	0.95	—
70	1.18	0.83	0.97	0.77
71	1.11	0.93	1.10	0.79
72	1.18	0.93	1.08	0.78
73	0.92	0.76	0.96	0.79
74	1.08	0.75	0.95	0.78
75	0.98	0.76	0.94	0.79
76	0.93	0.77	0.97	0.79
77	0.98	0.75	0.97	0.79
78	0.93	0.76	0.97	0.79
79	0.98	0.76	0.97	0.79
80	0.98	0.77	0.99	1.07
81	0.98	0.77	0.97	0.79
82	0.98	0.77	1.08	0.98
83	1.20	0.77	0.97	0.80
84	0.93	0.78	0.97	0.79
85	0.93	0.77	0.97	0.79
86	0.98	0.79	0.97	0.79
87	1.15	0.72	0.94	0.77
88	1.07	0.77	0.97	0.80
89	1.03	0.82	1.05	0.77
90	1.14	0.78	—	—
91	1.12	0.78	0.97	1.55
92	1.13	0.78	0.96	—
93	1.13	0.77	1.00	1.12
94	1.13	0.77	0.97	1.28
95	1.13	0.77	0.98	—
96	1.14	0.78	1.08	0.97
97	1.02	0.77	0.95	0.78
98	1.02	0.77	1.08	0.77
99	1.02	0.78	0.96	1.58
100	1.02	0.78	0.96	—
101	1.02	0.76	1.00	1.10
102	1.02	0.77	0.97	1.30
103	1.21	0.71	0.94	0.79
104	1.21	0.99	0.97	0.79
105	1.08	0.83	0.93	0.77
106	1.15	0.71	0.93	0.79
107	1.18	1.00	0.97	0.79
108	0.97	0.74	0.95	0.78
109	0.98	0.75	—	—
110	1.20	0.71	0.93	0.79
111	1.07	0.77	0.97	0.79
112	1.23	0.99	0.97	0.79
113	0.99	0.76	0.97	0.79
114	1.18	1.00	0.97	0.78
115	1.18	0.72	0.93	0.79
116	0.98	0.75	0.97	0.79
117	1.05	0.77	0.97	0.79
118	1.22	0.71	0.95	0.78
119	1.32	0.80	0.98	0.79
120	1.03	0.82	0.98	0.81
121	1.19	0.99	0.97	0.79
122	1.10	0.77	1.06	0.99
123	1.02	0.79	0.97	0.80
124	1.09	0.82	0.95	0.78
125	1.09	0.83	1.08	0.99
126	1.18	0.75	0.95	0.79
127	1.17	0.77	0.97	—
128	1.12	0.77	0.96	0.78
129	1.14	0.78	0.97	0.79
130	1.10	0.76	0.96	0.78
131	1.12	0.77	0.96	0.79
132	1.03	0.77	0.97	0.78
133	0.96	0.76	0.95	0.78
134	0.96	0.77	0.95	0.79
135	1.14	0.71	0.95	0.79
136	1.06	0.75	0.97	0.79
137	1.12	0.70	0.96	0.78
138	1.23	0.72	0.95	0.79
139	1.11	0.76	0.97	0.79
140	1.07	1.04	1.06	0.78
141	1.17	0.72	0.95	0.80
142	1.17	0.69	0.98	0.79
143	1.27	0.72	0.95	0.79
144	1.16	0.78	0.97	0.78

续表

化合物 \ 质子	19-H	18-H	21-H	27-H	化合物 \ 质子	19-H	18-H	21-H	27-H
145	1.13	0.81	0.93	0.78	**161**	1.05	0.77	1.05	1.06
146	1.17	0.75	0.97	0.79	**162**	0.98	0.68	0.98	0.79
147	1.22	0.75	0.95	0.78	**163**	0.97	0.68	1.02	0.77
148	1.62	0.92	1.13	0.70	**164**	1.00	0.68	0.98	0.79
149	1.50	0.84	1.13	0.71	**165**	0.99	0.68	1.02	0.78
150	1.30	0.77	—	—	**166**	0.97	0.68	0.98	0.78
151	1.23	0.77	0.95	0.78	**167**	0.98	0.68	1.00	0.78
152	1.30	0.78	0.97	0.78	**168**	0.99	0.70	1.00	0.78
153	1.01	0.76	0.95	0.78	**169**	0.97	0.66	0.97	0.78
154	1.03	0.77	0.96	0.79	**170**	1.00	0.70	1.02	0.77
155	1.16	0.78	0.96	0.78	**171**	0.97	0.82	0.98	0.78
156	1.03	0.80	—	—	**172**	1.00	0.83	1.07	0.78
157	1.17	0.76	—	—	**173**	0.99	0.82	0.98	0.78
158	0.98	0.85	—	—	**174**	1.00	0.83	1.07	0.78
159	1.26	0.71	—	—	**175**	0.98	0.85	0.99	0.78
160	1.22	0.91	0.97	0.79	**176**	1.01	0.90	1.13	0.78

表 11-5 甾体皂甙元化合物名称与编号对照表

编号	名称	编号	名称
1	5α,25D-螺旋甾烷	**31**	3β-羟基-5α,25D-螺旋甾烷-11-酮
2	5α,25D-螺旋甾烷-3-酮	**32**	3β,11β-二羟基-5α,25D-螺旋甾烷
3	5α,25D-螺旋甾-2-烯	**33**	11β-乙酰氧基-3β-羟基-5α,25D-螺旋甾烷
4	5α,25D-螺旋甾烷-3-酮	**34**	3β-羟基-5α,25D-螺旋甾烷-12-酮(海可皂甙元)
5	3α-羟基-5α,25D-螺旋甾烷	**35**	3β,12α-二羟基-5α,25D-螺旋甾烷
6	3β-羟基-5α,25D-螺旋甾烷(提果皂甙元)	**36**	3β,12β-二羟基-5α,25D-螺旋甾烷
7	3β-羟基-5α,25L-螺旋甾烷(新提果皂甙元)	**37**	3α-乙酰氧基-11β-羟基-5α,25D-螺旋甾烷
8	3α-乙酰氧基-5α,25D-螺旋甾烷	**38**	3β-乙酰氧基-25D-螺旋甾-4-烯
9	3β-乙酰氧基-5α,25D-螺旋甾烷(提果皂甙元乙酸酯)	**39**	3β-乙酰氧基-25D-螺旋甾-5-烯(薯蓣皂甙元乙酸酯)
10	3β-乙酰氧基-5α,25L-螺旋甾烷(新提果皂甙元乙酸酯)	**40**	3β,27-二乙酰氧基-25D-螺旋甾-5-烯(异纳尔索皂甙元乙酸酯)
11	1α,3β-二乙酰氧基-5α,25D-螺旋甾烷	**41**	3β-乙酰氧基-5α,25D-螺旋甾-9(11)-烯
12	5α,25D-螺旋甾-2-烯-11-酮	**42**	3β-乙酰氧基-5α,25D-螺旋甾烷-11-酮
13	11α-羟基-5α,25D-螺旋甾-2-烯	**43**	3β-乙酰氧基-23α-溴-5α,25D-螺旋甾烷-11-酮
14	2α,3β-二羟基-5α,25D-螺旋甾烷(吉托皂甙元)	**44**	3β-乙酰氧基-23β-溴-5α,25D-螺旋甾烷-11-酮
15	2α,3β-二羟基-5α,25L-螺旋甾烷(新吉托皂甙元)	**45**	3β-乙酰氧基-11β-羟基-5α,25D-螺旋甾烷
16	2α,3β-二乙酰氧基-5α,25D-螺旋甾烷(吉托皂甙元乙酸酯)	**46**	3β-乙酰氧基-5α,25D-螺旋甾烷-12-酮(海可皂甙元乙酸酯)
17	2α,3β-二乙酰氧基-5α,25L-螺旋甾烷(新吉托皂甙元乙酸酯)	**47**	3β-乙酰氧基-5α,25L-螺旋甾烷-12-酮(剑麻皂甙元乙酸酯)
18	2α,3α-环氧-11α-羟基-5α,25D-螺旋甾烷	**48**	3β,12α-二乙酰氧基-5α,25D-螺旋甾烷
19	25D-螺旋甾-4-烯-3-酮	**49**	3β,12β-二乙酰氧基-5α,25D-螺旋甾烷
20	5α,25D-螺旋甾烷-3,7-二酮	**50**	25D-螺旋甾-1,4-二烯-3-酮
21	5α,25D-螺旋甾烷-3,11-二酮	**51**	1β,3β-二乙酰氧基-25D-螺旋甾-5-烯(鲁斯可皂甙元二乙酸酯)
22	3α-羟基-5α,25D-螺旋甾烷-11-酮	**52**	2α,3α-二羟基-5α,25D-螺旋甾烷-11-酮
23	3β-羟基-25D-螺旋甾-4-烯	**53**	2α,3β-二羟基-5α,25D-螺旋甾烷-12-酮(门诺皂甙元)
24	3β-羟基-25D-螺旋甾-5-烯(薯蓣皂甙元)	**54**	2α,3β-二乙酰氧基-5α,25D-螺旋甾烷-12-酮(门诺皂甙元二乙酸酯)
25	3β-羟基螺旋甾-5,25(27)-二烯	**55**	25D-螺旋甾-4,6-二烯-3-酮
26	3β,27-二羟基-25D-螺旋甾-5-烯(异纳尔索皂甙元)	**56**	6α-甲基-25D-螺旋甾-4-烯-3-酮
27	3β-羟基-5α,25D-螺旋甾烷-6-酮(拉克索皂甙元)	**57**	7α-羟基-25D-螺旋甾-4-烯-3-酮
28	3β,6α-二羟基-5α,25D-螺旋甾烷(克洛皂甙元)		
29	3β,6β-二羟基-5α,25D-螺旋甾烷(β-克洛皂甙元)		
30	3β-羟基-5α,25D-螺旋甾-9(11)-烯		

续表

编号	名　　称
58	3β,4α,5α-三羟基-5α,25D-螺旋甾烷
59	3β-羟基-25D-螺旋甾-5-烯-12-酮(静特诺皂甙元)
60	3β,12α-二羟基-25D-螺旋甾-5-烯(亥洛尼皂甙元)
61	3β,17α-二羟基-25D-螺旋甾-5-烯(彭罗皂甙元)
62	3β-羟基-5α,25D-螺旋甾-9(11)-烯-12-酮
63	3β-乙酰氧基-7α-羟基-25D-螺旋甾-5-烯
64	3β-乙酰氧基-8β-氰基-5α,25D-螺旋甾烷-11-酮
65	3β-乙酰氧基-5α,25D-螺旋甾-9(11)-烯-12-酮
66	25D-螺旋甾-1,4-二烯-3,11-二酮
67	1α,2α-二羟基-25D-螺旋甾-4-烯-3-酮
68	1β,2β-二羟基-25D-螺旋甾-4-烯-3-酮
69	1α,2α-二乙酰氧基-25D-螺旋甾-4-烯-3-酮
70	1β,2β-二乙酰氧基-25D-螺旋甾-4-烯-3-酮
71	2α,3β-二羟基-5α,25D-螺旋甾-9(11)-烯-12-酮
72	2α,3β-二乙酰氧基-5α,25D-螺旋甾-9(11)-烯-12-酮
73	5β,25D-螺旋甾烷
74	5β,25D-螺旋甾烷-2-酮
75	5β,25D-螺旋甾-2-烯
76	2α-乙酰氧基-5β,25D-螺旋甾烷
77	2β-乙酰氧基-5β,25D-螺旋甾烷
78	3α-羟基-5β,25D-螺旋甾烷
79	3β-羟基-5β,25D-螺旋甾烷(异菝葜皂甙元)
80	3β-羟基-5β,25L-螺旋甾烷(菝葜皂甙元)
81	3β-乙酰氧基-5β,25D-螺旋甾烷(异菝葜皂甙元乙酸酯)
82	3β-乙酰氧基-5β,25L-螺旋甾烷(菝葜皂甙元乙酸酯)
83	5β,25D-螺旋甾烷-7-酮
84	7α-羟基-5β,25D-螺旋甾烷
85	7α-乙酰氧基-5β,25D-螺旋甾烷
86	7β-乙酰氧基-5β,25D-螺旋甾烷
87	5β,25D-螺旋甾烷-11-酮
88	11α-羟基-5β,25D-螺旋甾烷
89	11α-乙酰氧基-5β,25D-螺旋甾烷
90	1β,3β-二羟基-5β,25L-螺旋甾烷(万年青皂甙元)
91	1β,3β-二羟基-5β-螺旋甾-25(26)-烯
92	1β,3β-二羟基-5β-螺旋甾-25(27)-烯(欧铃兰皂甙元)
93	1β,3β,25β-三羟基-5β,25D-螺旋甾烷(异吉祥草皂甙元)
94	1β,3β,25β-三羟基-5β,25L-螺旋甾烷(吉祥草皂甙元)
95	1β,3β,27-三羟基-5β,25D-螺旋甾烷(异卡里亚皂甙元)
96	3β-乙酰氧基-1β-羟基-5β,25L-螺旋甾烷(万年青皂甙元乙酸酯)
97	1β,3β-二乙酰氧基-5β,25D-螺旋甾烷(异万年青皂甙元二乙酸酯)
98	1β,3β-二乙酰氧基-5β,25L-螺旋甾烷(万年青皂甙元二乙酸酯)
99	1β,3β-二乙酰氧基-5β-螺旋甾-24-烯
100	1β,3β-二乙酰氧基-5β-螺旋甾-25(27)-烯(欧铃兰皂甙元二乙酸酯)
101	1β,3β-二乙酰氧基-25β-羟基-5β,25D-螺旋甾烷(异吉祥草皂甙元二乙酸酯)
102	1β,3β-二乙酰氧基-25α-羟基-5β,25L-螺旋甾烷(吉祥草皂甙元二乙酸酯)
103	5β,25D-螺旋甾-2-烯-11-酮
104	11β-羟基-5β,25D-螺旋甾-2-烯
105	11α-乙酰氧基-5β,25D-螺旋甾-2-烯
106	2α-羟基-5β,25D-螺旋甾烷-11-酮
107	2α,11β-二羟基-5β,25D-螺旋甾烷
108	2β,3α-二羟基-5β,25D-螺旋甾烷(杨诺皂甙元)
109	2β,3β-二羟基-5β,25L-螺旋甾烷(马尔可皂甙元)
110	2β-羟基-5β,25D-螺旋甾烷-11-酮
111	2β,11α-二羟基-5β,25D-螺旋甾烷
112	2β,11β-二羟基-5β,25D-螺旋甾烷
113	2α,3β-二乙酰氧基-5β,25D-螺旋甾烷
114	11β-羟基-2α-乙酰氧基-5β,25D-螺旋甾烷
115	2α-乙酰氧基-5β,25D-螺旋甾烷-11-酮
116	2β,3α-二乙酰氧基-5β,25D-螺旋甾烷(杨诺皂甙元二乙酸酯)
117	2β,3β-二乙酰氧基-5β,25D-螺旋甾烷(沙莫皂甙元二乙酸酯)
118	2β-乙酰氧基-5β,25D-螺旋甾烷-11-酮
119	5β,25D-螺旋甾烷-3,7-二酮
120	7α-羟基-5β,25D-螺旋甾烷-3-酮
121	3α-乙酰氧基-11β-羟基-5β,25D-螺旋甾烷
122	3β,11α-二羟基-5β,25L-螺旋甾烷(新诺吉拉皂甙元)
123	3β-乙酰氧基-7β-羟基-5β,25D-螺旋甾烷
124	3β,11α-二乙酰氧基-5β,25D-螺旋甾烷(诺吉拉皂甙元二乙酸酯)
125	3β,11α-二乙酰氧基-5β,25L-螺旋甾烷(新诺吉拉皂甙元二乙酸酯)
126	2β,3α-二乙酰氧基-5β,25D-螺旋甾烷-1-酮
127	1α,2β,3α-三羟基-5β,25D-螺旋甾烷
128	1β,2β,3α-三羟基-5β,25D-螺旋甾烷(托可皂甙皂元)
129	3α-乙酰氧基-1β,2β-二羟基-5β,25D-螺旋甾烷(托可皂甙元乙酸酯)
130	2β-乙酰氧基-1β3α 二羟基-5β,25D-螺旋甾烷(托可皂甙元乙酸酯)
131	2β,3α 二乙酰氧基-1β,-羟基-5β,25D-螺旋甾烷(托可皂甙元二乙酸酯)
132	1α,2β,3α-三乙酰氧基-5β,25D-螺旋甾烷
133	1β,3α-二乙酰氧基-2β-羟基-5β,25D-螺旋甾烷
134	1β,2β,3α-三乙酰氧基-5β,25D-螺旋甾烷(托可皂甙元三乙酸酯)
135	2α,3α-二羟基-5β,25D-螺旋甾烷-11-酮
136	2α,3α,11α-三羟基-5β,25D-螺旋甾烷
137	2β,3β-二羟基-5β,25D-螺旋甾-9(11)-烯
138	2β,3β-二羟基-5β,25D-螺旋甾烷-11-酮
139	2β,3β,11α-三羟基-5β,25D-螺旋甾烷(米他皂甙元)
140	2β,3β-二羟基-5β,25D-螺旋甾烷-12-酮(美克索皂甙元)
141	2α,3α-二乙酰氧基-5β,25D-螺旋甾烷-11-酮
142	2β,3β-二乙酰氧基-5β,25D-螺旋甾-9(11)-烯

续表

编号	名称	编号	名称
143	2β,3β-二乙酰氧基-5β,25D-螺旋甾烷-11-酮	159	11-甲烯基-5α,22α-螺旋甾烷-3-酮
144	2β,3β-二乙酰氧基-11α-羟基-5β,25D-螺旋甾烷(米他皂甙元二乙酸酯)	160	螺旋甾-1,4,6-三烯-3-酮
145	2β,3β,11α-三乙酰氧基-5β,25D-螺旋甾烷(米他皂甙元三乙酸酯)	161	2β,3β-二乙酰氧基-5β,25L-螺旋甾烷(马尔可皂甙元二乙酸酯)
146	2β,3α-二乙酰氧基-5β,25D-螺旋甾烷-1-酮	162	3β,12α-二羟基-5α,25D-螺旋甾-9(11)-烯
147	3β,4β-二乙酰氧基-5β-羟基-5β,25D-螺旋甾烷-1-酮	163	3β,12β-二羟基-5α,21α,25D-螺旋甾-9(11)-烯
148	1α,2β,3α,5β-四羟基-5β,25D-螺旋甾烷	164	3β-乙酰氧基-12α-羟基-5α,25D-螺旋甾-9(11)-烯
149	1β,2β,3α,5β-四乙酰氧基-5β,25D-螺旋甾烷(柯凯皂甙元)	165	3β-乙酰氧基-12β-羟基-5α,21α,25D-螺旋甾-9(11)-烯
150	1β,3β,4β,5β-四羟基-5β,25D-螺旋甾烷(凯提皂甙元)	166	3β-羟基-12α-甲氧基-5α,21α,25D-螺旋甾-9(11)-烯
151	2β,3α-二乙酰氧基-1β,5β-二羟基-5β,25D-螺旋甾烷(柯凯皂甙元二乙酸酯)	167	3β-羟基-12β-甲氧基-5α,25α,25D-螺旋甾-9(11)-烯
152	3β,4β-二乙酰氧基-1β,5β-二羟基-5β,25D-螺旋甾烷(凯提皂甙元二乙酸酯)	168	3β-羟基-12β-乙氧基-5α,21α,25D-螺旋甾-9(11)-烯
153	1α,2β,3α-三乙酰氧基-5β-羟基-5β,25D-螺旋甾烷	169	3β-乙酰氧基-12α-乙氧基-5α,21α,25D-螺旋甾-9(11)-烯
154	1β,2β,3α-三乙酰氧基-5β-羟基-5β,25D-螺旋甾烷(柯凯皂甙元三乙酸酯)	170	3β-乙酰氧基-12β-乙氧基-5α,21α,25D-螺旋甾-9(11)-烯
155	1β,3β,4β-三乙酰氧基-5β,25D-螺旋甾烷(凯提皂甙元三乙酸酯)	171	3β-羟基-12α-氯-5α,21α,25D-螺旋甾-9(11)-烯
156	5α,22α-螺旋甾烷-3-酮	172	3β-羟基-12β-氯-5α,21α,25D-螺旋甾-9(11)-烯
157	5α,22α-螺旋甾-9(11)-烯-3-酮	173	3β-乙酰氧基-12α-氯-5α,21α,25D-螺旋甾-9(11)-烯
158	5α,22α-螺旋甾-11-烯-3-酮	174	3β-乙酰氧基-12β-氯-5α,21α,25D-螺旋甾-9(11)-烯
		175	3β-乙酰氧基-12α-溴-5α,21α,25D-螺旋甾-9(11)-烯
		176	3β-乙酰氧基-12β-溴-5α,21α,25D-螺旋甾-9(11)-烯

第二节 木脂素类化合物的^{1}H-NMR化学位移

表 11-6 木脂素类化合物 177～181 的^{1}H-NMR化学位移[12]

质子 \ 化合物	177	178	179	180	181
4-H	6.43s	6.30s	6.39s	6.40s	6.72s
6-H$_a$	2.0～2.5m	2.0～2.5m	2.0～2.5m	2.0～2.5m	2.0～2.5m
6-H$_b$	2.0～2.5m	2.0～2.5m	2.0～2.5m	2.0～2.5m	2.0～2.5m
7-H	1.98m	1.78m	1.88m	1.92m	2.14m
9-H	5.85s	5.70s	5.87s	5.58s	5.90s
11-H	6.76s	6.72s	6.76s	6.44s	6.82s
7-CH$_3$	1.13d(7)	1.04d(7)	1.08d(7)	1.10d(7)	1.16d(7)
8-CH$_3$	1.24s	1.16s	1.12s	1.20s	1.30s
O—CH$_2$—O—	5.72s	5.82s	5.87s	5.92s	
	5.66s	5.78s	5.82s	5.70s	
				5.56s	
OCH$_3$	3.78s	3.80s	3.78s	3.70s	3.90s
OCH$_3$	3.64s	3.68s	3.68s	3.18s	3.86s
OCH$_3$	3.46s	3.56s	3.41s	—	3.50s
OCH$_3$	3.24s	3.40s	3.37s	—	3.30s
					3.10s
OH	1.47s(3H)	1.46br(3H)	1.12s(3H)	1.20s(3H)	1.30s(3H)
—COR	—	1.78d(7)	1.64d(7)	—	—
	—	5.80m	5.84q(7)	—	—
	—	1.30q(1.5)	1.54s	—	—

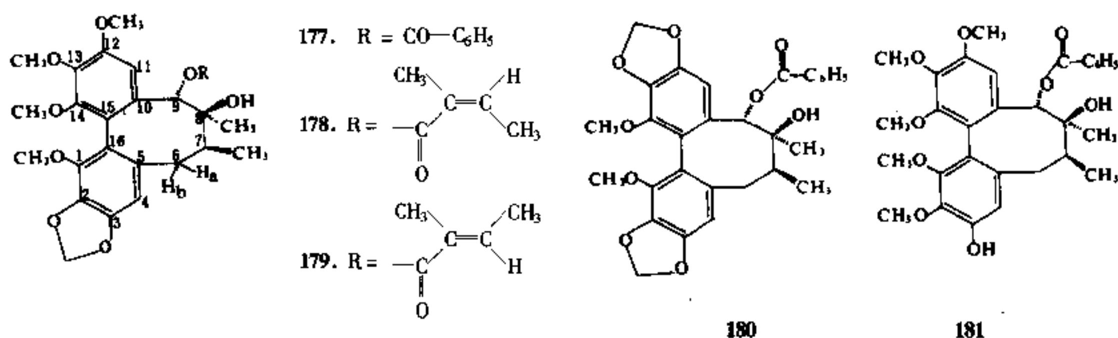
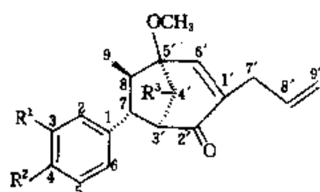


表 11-7 木脂素类化合物 182～186 的 ^{1}H-NMR 化学位移①[72]

质子 \ 化合物	182	183	184	185	186
2-H	6.59,d(1.8)	6.57,d(2.1)	7.12,d(2.4)		7.09,s
5-H	6.85,d(8.7)	6.79,d(8.4)	6.75,d(8.4)	6.83～6.87,m	6.69,d(8.1)
6-H	6.62,dd(8.1,1.8)	6.66,dd(2.1,8.4)	6.86,dd(2.4,8.4)		6.77,d(8.1)
7-H	2.45,d(5.1)	2.46,d(4.5)	2.37,d(8.1)	2.43,d(7.5)	2.34,d(8.1)
8-H	2.40,m	2.45,m	2.66,dq(6.9,8.1)	2.76,dq(6.9,7.5)	2.62,dd(6.9,8.1)
9-H	1.07,d(6.3)	1.07,d(6.0)	1.00,d(6.9)	1.01,d(6.9)	0.97,d(6.9)
3'-H	3.51,s	3.53,s	3.07,s	3.00,s	3.05,s
4'-H			4.20,s	5.31,s	4.18,s
6'-H	7.04,s	7.05,s	6.84,s	6.81,s	6.83,s
7'-H	3.11,m	3.11,m	3.02,m	3.04,dd(6.6,11.1)	2.90～3.08,m
8'-H	5.85,m	5.85,m	5.83,m	5.83,m	5.85,m
9'-H	5.17,m	5.18,m	5.13,d(15)	5.15,d(13.2)	5.12,m
3-OCH$_3$	3.87,s	3.86,s	3.85,s	3.86,s	
4-OCH$_3$		3.86,s	3.85,s	3.87,s	
5'-OCH$_3$	3.64,s	3.64,s	3.44,s	3.37,s	3.44,s
OCH$_2$O					5.92,s
4'-OAc				2.17,s	

① 括号内数据为偶合常数值。



182. $R^1 = OCH_3$, $R^2 = OH$, $R^3 = O$

183. $R^1 = R^2 = OCH_3$, $R^3 = OH$

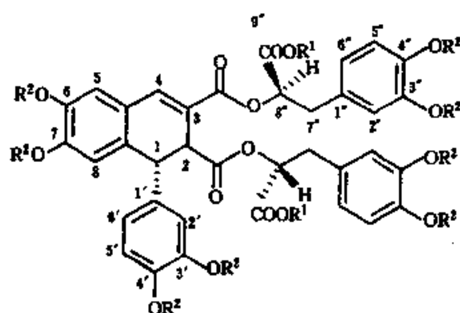
184. $R^1 = R^2 = OCH_3$, $R^3 = O$

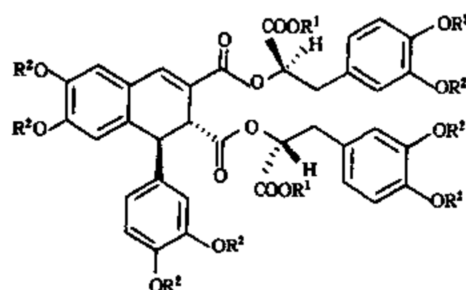
185. $R^1 = R^2 = OCH_3$, $R^3 = OAc$

186. $R^1R^2 = O—CH_2—O$, $R^3 = OH$

表 11-8 木脂素类化合物 187～193 的^{1}H-NMR 化学位移[73]

质子＼化合物	187	188	189	190	191	192	193
1-H					4.55br s	4.18br s	4.66br s
2-H	4.01d(1.5)	4.04d(1.5)	4.06br s	3.98d(1.5)	3.93d(1.5)	3.94d(1.5)	4.07br s
4-H	7.64s	7.62s	7.62s	7.78s	7.65s	7.64s	7.67s
5-H	6.93s	6.92s	6.93s	7.01s	6.95s	6.93s	7.10s
8-H	6.72s	6.68s	6.67s	6.33s	6.60s	6.47s	6.95s
2′-H	6.63d(2)	6.59d(2)	6.59d(2)	6.60d(2)	6.46d(2)	6.51d(2)	6.71d(2)
5′-H	6.69d(8)	6.68d(8)	6.68d(8)	6.63d(8)	6.68d(8)	6.65d(8)	6.69d(8)
6′-H	6.42dd(2,8)	6.37dd(2,8)	6.36dd(2,8)	6.18dd(2,8)	6.30dd(2,8)	6.32dd(2,8)	6.50dd(2,8)
2″-H	6.79,6.90d(2)	6.77,6.88d(2)	6.75,6.87d(2)	6.89,6.93d(2)	6.80,6.86d(2)	6.81,6.82d(2)	6.80,6.91d(2)
5″-H	6.73,6.76d (8)	6.70,6.72d (8)	6.69,6.71d (8)	6.76,6.90d (8)	6.75,6.76d (8)	6.73,6.80d (8)	6.71,6.75d (8)
6″-H	6.53,6.64dd (2,8)	6.44,6.54dd (2,8)	6.41,6.52dd (2,8)	6.70,6.78dd (2,8)	6.59,6.63dd (2,8)	6.60,6.63dd (2,8)	6.54,6.64dd (2,8)
7″-H	2.82～3.15m	2.75～3.35m	2.72～3.15m	2.89～3.21m	2.98～3.06m	2.87～3.04m	2.80～3.15m
8″-H	4.84,4.98dd (3,9.5)	4.81,4.98dd (3,9.5)	4.83,5.02brd (10)	4.77,4.86brd (10.5)	5.00t(6.5) 5.04dd(5,7.5)	4.97dd(4,9) 5.09t(6)	4.87,5.00dd (3,10),5.09d(8)
端基-H							





187. R^1 = K, R^2 = H

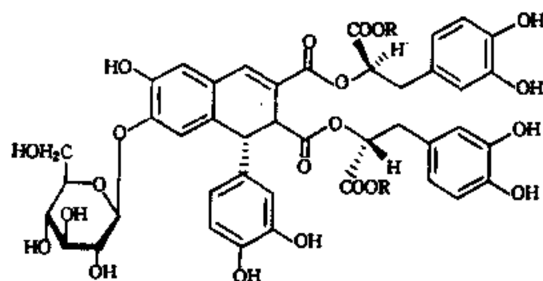
188. R^1 = Na、H, R^2 = H

189. R^1 = K(Na)、H, R^2 = H

192. R^1 = H, R^2 = H

190. R^1 = K(Na)、H, R^2 = H

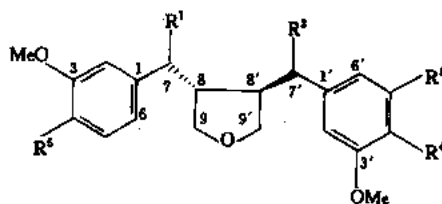
191. R^1 = CH, R^2 = CH_3



193. R = K 或 Na

表 11-9　木脂素类化合物 194 ~ 198 的 ^{1}H-NMR 化学位移[74]

质子 \ 化合物	194	195	196	197	198
2'-H	6.68s	6.94d (1.8)	6.92d (1.9)	6.70s	6.83d (1.8)
5'-H	—	7.01d (7.8)	7.05d (8.1)	—	7.13d 重叠
6'-H	6.68s	6.87dd (8.2,1.8)	6.82dd (8.0,1.9)	6.70s	6.70dd (8.1,1.9)
2-H	6.46d (1.9)	6.72d (1.8)	6.45d (1.9)	6.52m	7.04d (1.9)
5-H	6.97d (8.0)	6.92d (7.8)	6.94d (8.1)	6.95d (8.5)	6.95d (8.0)
6-H	6.56dd (1.9,8.0)	6.62dd (7.9,1.8)	6.55dd (8.2,1.8)	6.52m	7.13d 重叠
7α-H	2.40dd (12.7,10.3)	4.05d (8.2)	2.37dd (12.9,10.4)	2.20 ~ 2.60m	4.09 (8.4)
7β-H	2.74dd (12.6,4.5)		2.78dd (12.9,4.6)	2.20 ~ 2.60m	
7'-H	4.93d (6.1)	4.63d (7.50)	4.86d (6.2)	4.87d (5.4)	4.57d (8.8)
8-H	2.60m	2.57m	2.59m	2.20 ~ 2.60m	2.25m
8'-H	2.45m	2.04m	2.22m	2.20 ~ 2.60m	2.26m
9α-H	3.48dd (6.2,8.6)	4.07dd (8.8,7.6)	3.42dd (6.8,8.5)	3.70dd (6.3,8.6)	3.96dd (7.0,9.2)
9β-H	3.52dd (6.1,8.5)	4.37dd (8.9,4.8)	3.51dd (8.5,7.0)	3.99dd (6.2,8.6)	4.56dd (9.1,4.0)
9'α-H	3.82dd (11.0,7.0)	3.28dd (6.7,7.1)	3.80dd (6.4,10.4)	4.01dd (7.3,11.3)	3.81dd (6.0,9.0)
9'β-H	4.09dd (6.3,11.0)	3.08dd (7.0,9.2)	4.05dd (6.5,8.6)	4.30dd (6.4,11.3)	3.81dd (6.0,9.0)
OMe	3.37s(×2), 3.18s	3.17s,3.21s	3.13s,3.16s	3.36s(×2), 3.30s	3.42s,3.43s
OH/OAc	1.40s,5.34s, 5.38s	1.58s,5.61s	5.36s,5.44s	1.70s,1.93s, 2.00s	1.56s,1.85s, 1.88s
CH_3CH_2O—	—	1.05t (6.1)	—	—	1.03t (6.1)
CH_3CH_2O—	—	3.18m 重叠	—	—	3.22q(6.9) 3.05q(6.9)



194. R^1 = H, R^2 = R^4 = R^5 = OH, R^3 = OMe

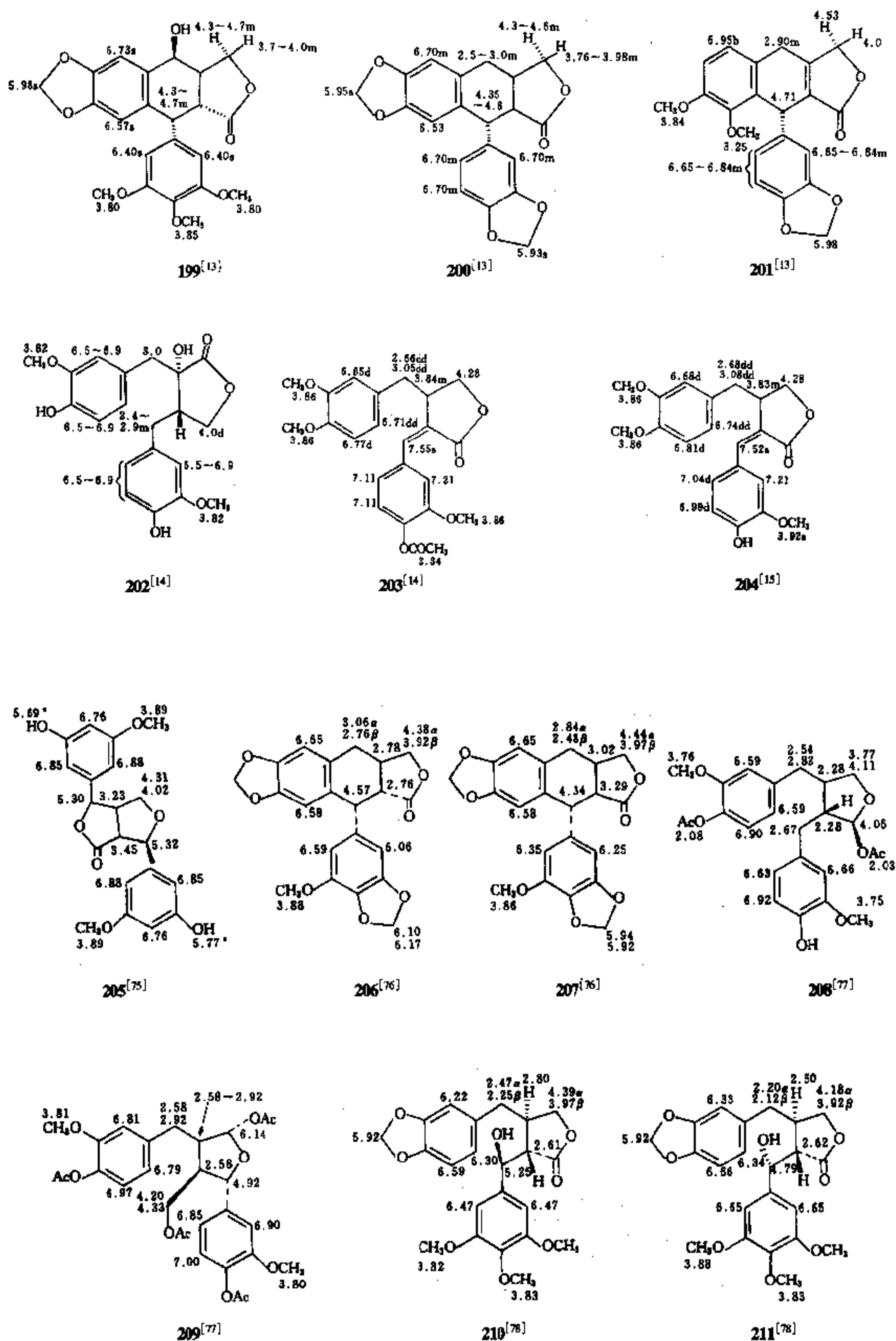
195. R^1 = OEt, R^2 = R^4 = R^5 = OH, R^3 = H

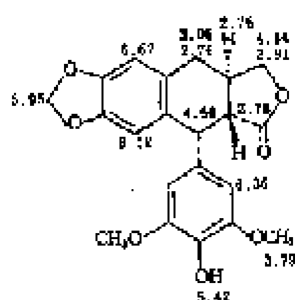
196. R^1 = H, R^2 = R^4 = R^5 = OH, R^3 = H

197. R^1 = H, R^2 = R^4 = R^5 = OAc, R^3 = OMe

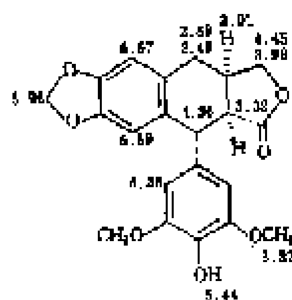
198. R^1 = OEt, R^2 = R^4 = R^5 = OAc, R^3 = H

其他天然木脂素类化合物 199～214 的^{1}H-NMR 化学位移如下：

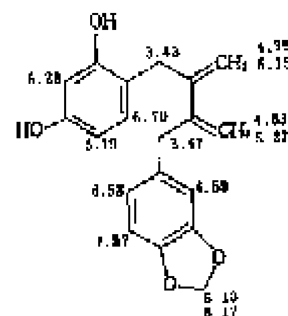




212[79]



213[79]



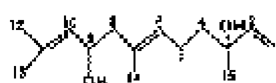
214[80]

第三节　天然烯炔类化合物的¹H-NMR化学位移

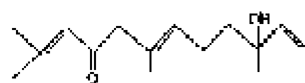
一、天然多烯类化合物的¹H-NMR化学位移

表 11-10　天然多烯类化合物 215～218 的¹H-NMR 化学位移[26]

质子＼化合物	215	216	217	218	质子＼化合物	215	216	217	218
$1-H_E$	5.22dd(1.5,17)	5.24dd	4.15bd	4.59bd	10-H	5.17bd(7)	6.10bs	5.39bd	5.34bd
$1-H_Z$	5.07dd(1.5,10.5)	5.08dd	4.15bd	4.59bd	12-H	1.67bs	1.89d	1.61bs	1.63bs
2-H	5.91(10.5,17)	5.92dd	5.14bt	5.12bt	13-H	1.72d	2.15d	1.71bs	1.71bs
6-H	5.28bt(7)	5.28bt	5.14bt	5.14bt	14-H	1.69d	1.62bs	1.71bs	1.71bs
9-H	4.45dt(7)	—	5.62dt	5.62dt	15-H	1.29s	1.30s	1.71bs	1.71bs



215



216

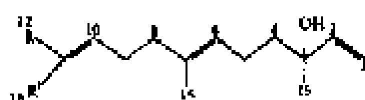


217. R = H

218. R = $COCH_3$

表 11-11　天然多烯类化合物 219～223 的¹H-NMR 化学位移[17]

质子＼化合物	219	220	221	222	223	质子＼化合物	219	220	221	222	223
$1-H_E$	5.21dd	5.20dd	5.22dd	5.18dd	5.22dd	10-H	5.37tq	5.25tq	6.44tq	5.30tq	6.46tq
$1-H_Z$	5.06dd	5.06dd	5.08dd	5.08dd	5.07dd	12-H	1.77dt	1.79dt	1.78dt	3.97bs	9.39s
2-H	5.97dd	5.90dd	5.92dd	5.87dd	5.92dd	13-H	4.66bs	4.10bs	10.11s	1.68bs	1.75bd
4-H	1.57m	1.60m	1.66m	1.60m	1.57m	14-H	1.59bs	1.59bs	1.62bs	1.60bs	1.64bs
5-H	2.00m	2.02dt	2.04m	2.10m	2.06m	15-H	1.29s	1.27s	1.29s	1.24s	1.29s
6-H	5.14tq	5.14tq	5.18tq	5.21tq	5.19tq	OCOR	6.06qq	—	—	—	—
8-H	2.00bt	2.00bt	2.15bt	2.10m	2.17bt		1.99dq	—	—	—	—
9-H	2.19dt	2.15dt	2.66dt	2.18dt	2.46dt		1.90dq	—	—	—	—

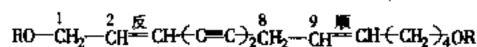


取代基＼化合物	219	220	221	222	223
R	CH_3	CH_3	CH_3	CH_2OH	CHO
R^1	$CH_2O-\overset{\overset{O}{\|}}{C}-O-\underset{CH_3}{\overset{CH_3}{C}}-H$	CH_2OH	CHO	CF_3	CH_3

二、天然烯炔类化合物的¹H-NMR化学位移

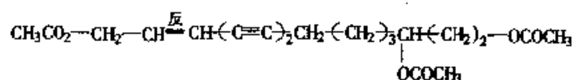
表 11-12　天然烯炔类化合物 224～231 的¹H-NMR 化学位移[18]

质子＼化合物	224	225	226	227	228	229	230	231
1-2H	4.24dd	4.62dd	4.60dd	4.62dd	4.63dd	4.62dd	4.64dd	4.65dd
2-H	6.37dt	6.27dt	6.33dt	6.31dt	6.31dt	6.28dt	6.30dt	6.29dt
3-H	5.79dt	5.76bd	5.73bd	5.75bd	5.82bd	5.81bd	5.84bd	5.84bd
8-H	3.07bd	3.07bd	2.46t	5.53m	5.76d	5.56bd	5.57bd	5.70d
9-H	5.45m	5.47m	1.82m	1.6m	6.19dd	6.28dt	6.70dd	6.67dd
10-H	5.45m	5.47m	1.41m	1.43m	5.29dt	2.19dt	6.14dd	6.31dd
11-H	2.09dt	2.09dt	1.69m	1.43m	1.64m	1.87dt	5.87dt	5.76dd
12-H	1.61m	1.64m	4.95m	1.43m	1.39m	4.97tt	2.24dt	5.41dt
13-H	1.61m	1.64m	1.69m	1.6m	1.64m	1.69m	1.76tt	1.98m
14-H	3.66t	4.07t	4.05t	4.05t	4.05t	4.08t	4.07t	4.11t
$OCOCH_3$	—	2.08s	2.07s	2.07s	2.09s	2.09s	2.09s	2.09s
	—	2.05s	2.05s	2.07s	2.07s	2.06s	2.06s	2.07s
	—	—	2.04s	2.07s	2.05s	2.06s	—	2.05s

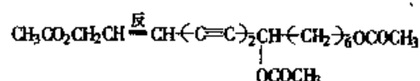


224. R—H

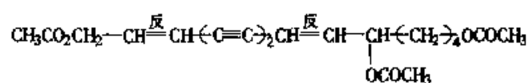
225. R—$COCH_3$



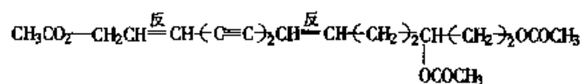
226



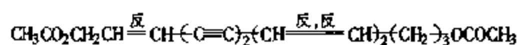
227



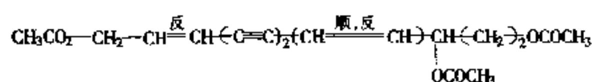
228



229



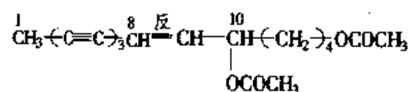
230



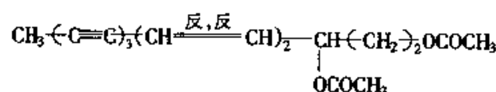
231

表 11-13 天然烯炔类化合物 232～240 的^{1}H-NMR 化学位移[18]

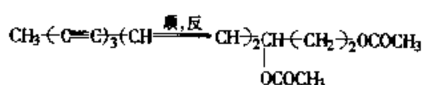
质子＼化合物	232	233	234	235	236	237	238	239	240
1-H	2.00s	2.01s	2.02s	2.00s	2.00s	2.01s	2.00s	2.01s	2.00s
8-H	5.71bd	5.66bd	5.51dd	5.66d	5.66d	5.52d	5.51d	—	—
9-H	6.23dd	6.71dd	6.53dd	6.76dd	6.72dd	6.57dd	6.54dd	—	—
10-H	5.28ddt	6.50dd	6.75dd	6.43dd	6.36dd	6.88dd	6.81dd	5.89dd	5.92dd
11-H	1.64m	5.75dd	5.89dd	5.84dd	5.80dd	5.93dd	5.90dd	6.39dd	6.37dd
12-H	1.64m	5.41dt	5.46dt	4.48m	5.36m	4.52m	5.36m	4.52m	4.48m
13-H	1.64m	1.89m	2.0m	4.02dd	3.72m	4.02dd	3.72m	3.80m	4.02dd
				4.19dd		4.20dd			4.19dd
14-H	4.05t	4.09t	4.12t	—	—	—	—	—	—
OCOCH$_3$	2.06s	2.01s	2.10s	2.10s	2.12	2.12s	2.14s	—	2.10s
	2.07s	2.07s	2.07s	—	—	—	—	—	—



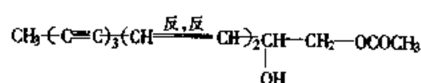
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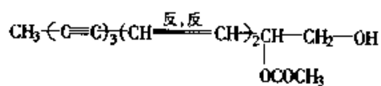
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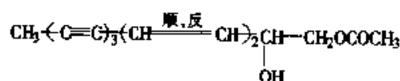
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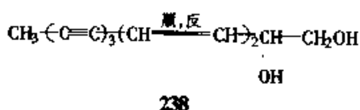
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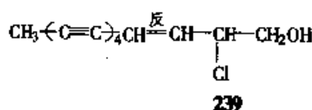
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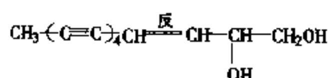
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238



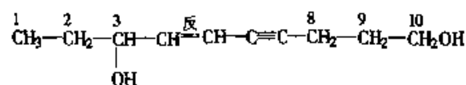
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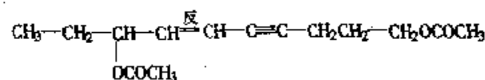
240

表 11-14 天然烯炔类化合物 241～248 的^{1}H-NMR 化学位移[18]

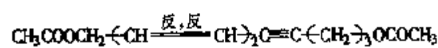
质子＼化合物	241	242	243	244	245	246	247	248
1-H	0.94t	0.90t	4.61bd	4.62dd	4.84dd	4.65dd	4.85dd	5.19s
2-H	1.57dq	1.65dq	5.80dt	6.28dt	6.13dt	6.32dt	6.17dt	—
		1.64dq						
3-H	4.08ddt	5.18ddt	6.29dd	5.77bd	5.69dt	5.83dt	5.76bd	7.11d
4-H	6.06dd	5.95dd	6.50dd	—	—	—	—	6.94d
5-H	5.68ddt	5.67ddt	5.63bd	—	—	—	—	—
8-H	2.45dt	2.42dt	2.44dt	2.44t	2.46t	5.83dt	5.83dt	4.91s
9-H	1.80tt	1.86tt	1.87tt	1.89tt	1.90tt	6.32dt	6.32dt	—
10-H	3.77t	4.16t	4.17t	4.16t	4.17t	4.65dd	4.65dd	—
COCH$_3$	—	2.06s	2.09s	2.09s	2.09s	2.10s	2.10s	2.09s
	—	2.06s	2.06s	2.07s	2.07s	2.10s	2.10s	2.13s



241



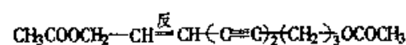
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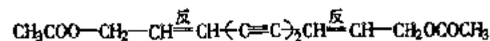
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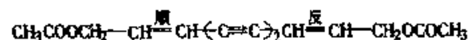
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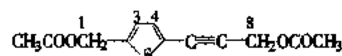
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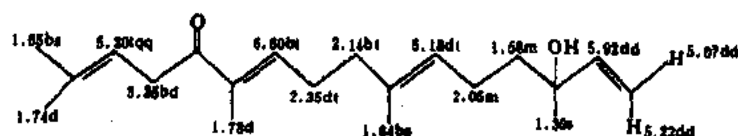
246



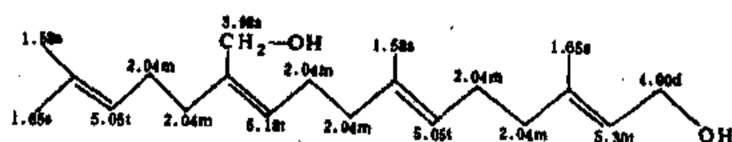
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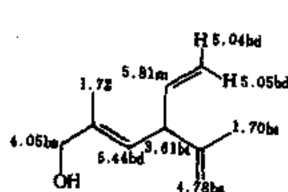
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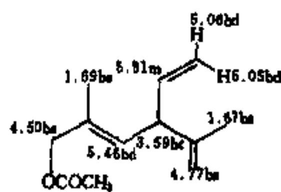


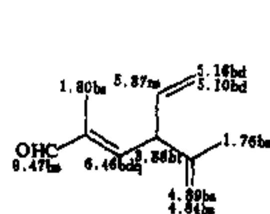
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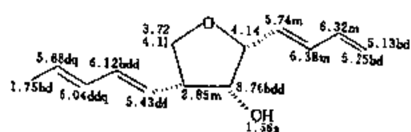
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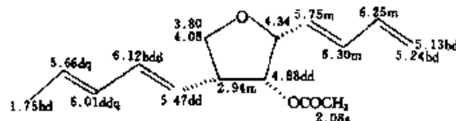




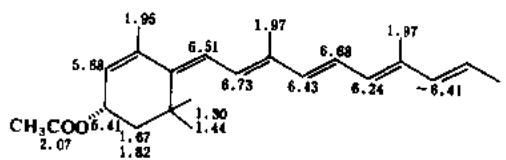
251[21] 252[21] 253[21]



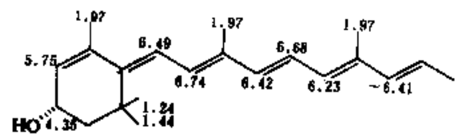
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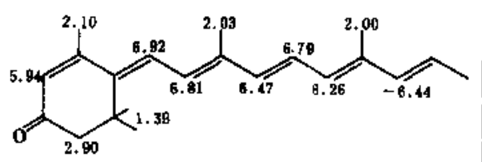
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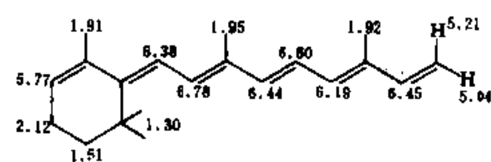
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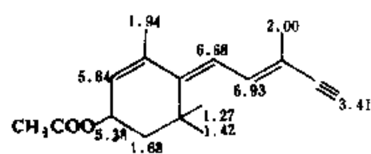
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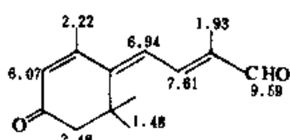
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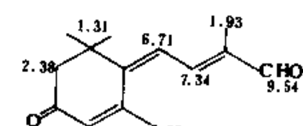
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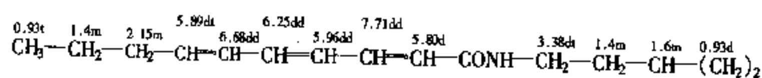
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261[22]



262[22]

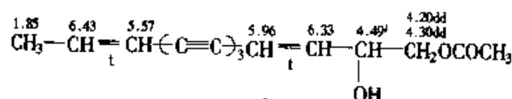


263[22]

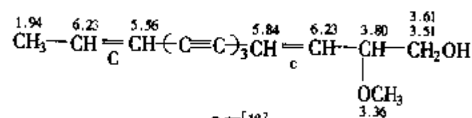


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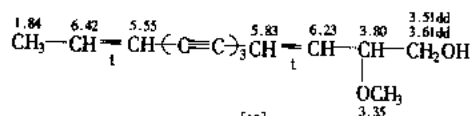
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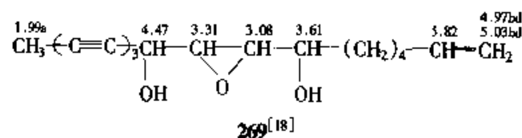
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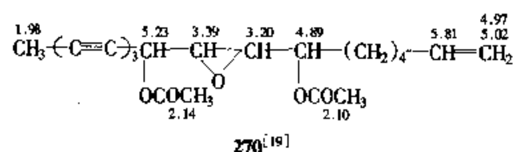
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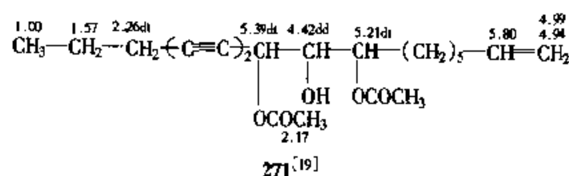


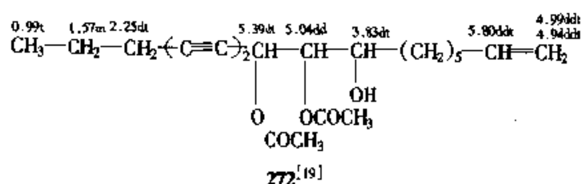
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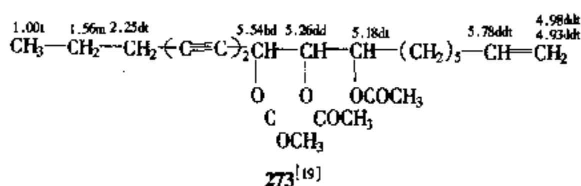


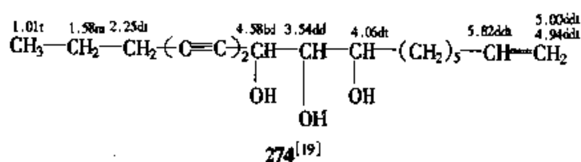
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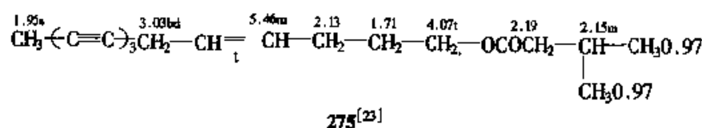

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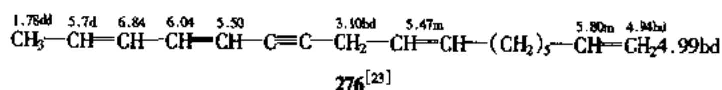

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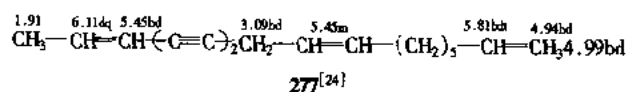

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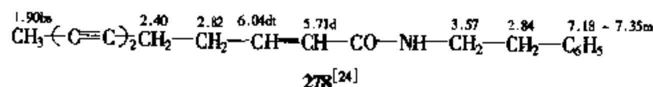

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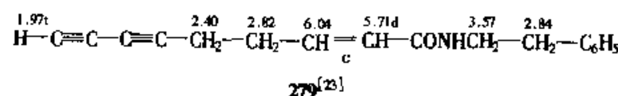

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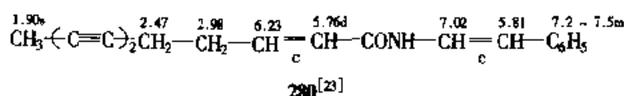

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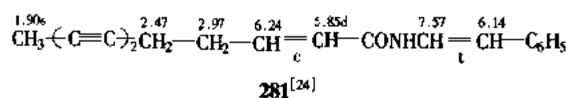

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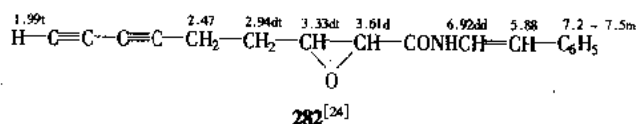

278[24]


279[23]

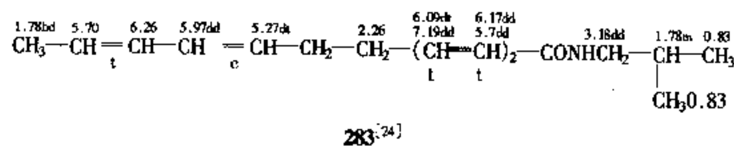

280[23]



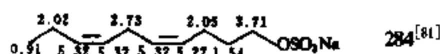
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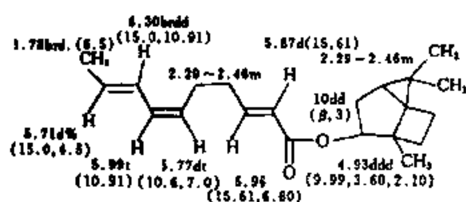
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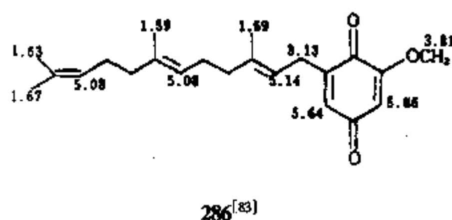
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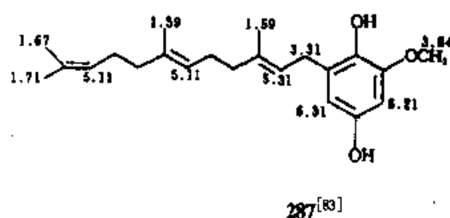
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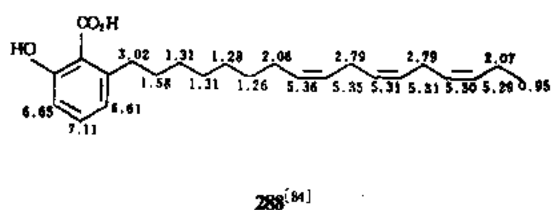
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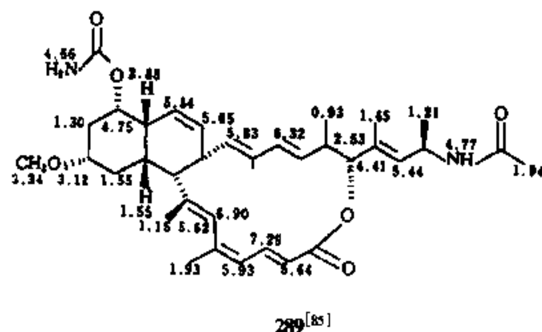
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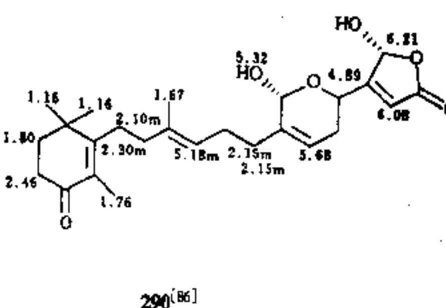
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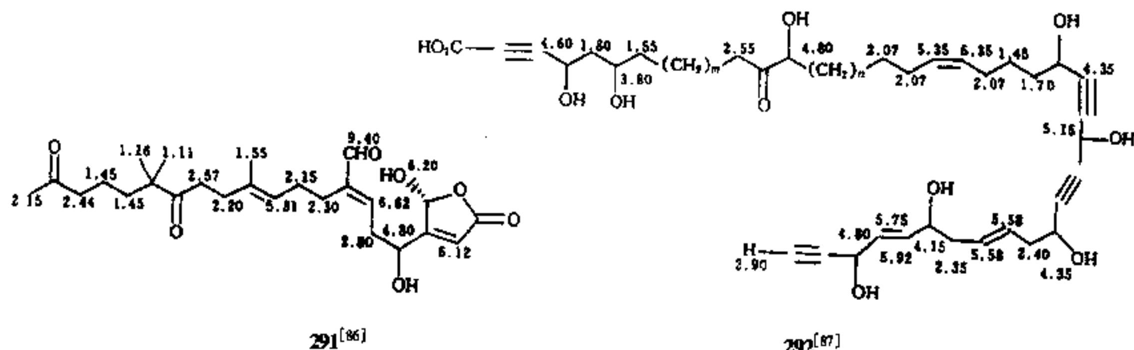
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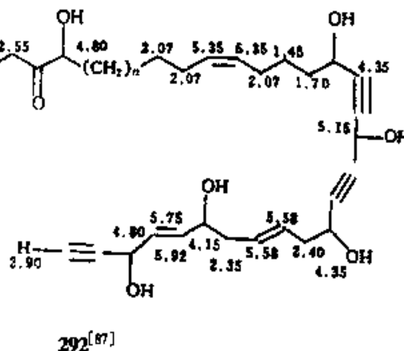


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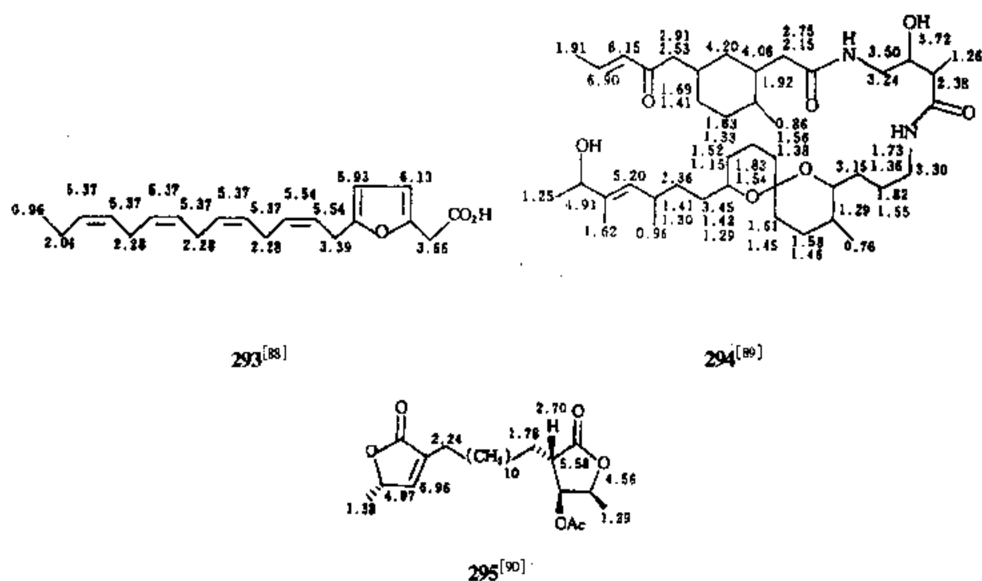
290[86]





291[86]

292[87]



293[88]

294[89]

295[90]

第四节 糖类化合物的^{1}H-NMR化学位移和偶合常数

一、五碳吡喃糖衍生物的^{1}H-NMR化学位移和偶合常数

表 11-15 五碳吡喃糖衍生物的^{1}H-NMR化学位移和 $J_{1,2}$值[25~28]

化合物	质子化学位移						$J_{1,2}$
	1-H	2-H	3-H	4-H	5a-H	5b-H	
α-木糖	5.26	3.63					3.1
β-木糖	4.65	3.26	3.49	3.58	3.36	4.00	7.4
α-D-木糖四乙酸酯							3.5
β-D-木糖四乙酸酯							6.9
β-D-木糖-1-硫缩醛吡喃糖全乙酰化物	5.38	5.00	5.22	4.92	3.53	4.16	8.1
α-来苏糖(α-Lyxose)	5.08	3.90					4.2
β-来苏糖	4.94	4.04			3.32	4.09	1.5
α-D-来苏糖四乙酸酯							2.9
β-D-来苏糖四乙酸酯							2.0
α-阿拉伯糖	4.60	3.58	3.72	4.04			7.2
β-阿拉伯糖	5.34	3.93	3.93	4.07			2.7
α-D-阿拉伯糖四乙酸酯							6.3
β-D-阿拉伯糖四乙酸酯							2.7
α-L-阿拉伯糖-1-硫缩醛吡喃糖全乙酰化物	5.35	5.19	5.11	5.26	3.47	3.96	7.0
α-核糖	4.91	3.85					2.1
β-核糖	4.99	3.60	4.13	3.79			6.4
α-D-核糖四乙酸酯							3.7
β-D-核糖-1-硫缩醛吡喃糖全乙酰化物	5.62	5.06	5.49	5.07	3.83	3.98	7.7
β-D-核糖四乙酸酯							4.8
2,3,4-三苯甲酰基-β-D-核吡喃糖氟化物	5.88		5.59~5.90		4.31	4.31	1.5
2,3,4-三苯甲酰基-β-D-核吡喃糖氯化物	6.34	5.70	6.03	5.7	4.38	4.38	1.7
2,3,4-三苯甲酰基-β-D-核吡喃糖碘化物	7.06	5.77	6.12	5.75	4.18	4.18	1.0
2,3,4-三苯甲酰基-β-D-核吡喃糖甲基甙	4.96	5.51	5.79	5.56	4.09	4.09	2.5
2,3,4-三苯甲酰基-β-D-核吡喃糖苄基醚	5.20	5.59	5.86	5.6	4.17	4.17	2.4
2,3,4-三苯甲酰基-α-D-核吡喃糖氟化物	5.81	5.28	6.16	5.44	4.19	4.19	3.3

续表

化合物	质子化学位移						$J_{1,2}$
	1-H	2-H	3-H	4-H	5a-H	5b-H	
2,3,4-三苯甲酰基-α-D-核吡喃糖氯化物	6.33	5.46	6.16	5.42	4.20	4.20	4.4
2,3,4-三苯甲酰基-α-D-核吡喃糖溴化物	6.53	5.47	6.25	5.52	4.27	4.27	4.4
α-D-核吡喃糖四苯甲酸酯	6.60	5.66	6.20	5.52	4.22	4.22	3.7
β-D-核吡喃糖四苯甲醛酯	6.63	5.74	6.04	5.72	4.30	4.30	3.5
2,3,4-三苯甲酰基-β-D-核吡喃糖氰化物	5.04	5.66	6.10	5.56	4.22	4.22	6.7
2,3-脱水-β-D-核吡喃糖甲基甙	4.84	3.56	3.20	3.6~4.0	3.6~4.0	3.6~4.0	0
2,3-脱水-β-L-核吡喃糖甲基甙	4.85	3.52	3.17	3.5~3.95	3.5~3.95	3.5~3.95	0

表 11-16　五碳吡喃糖衍生物的偶合常数[25-28]

化合物 \ 偶合常数	J_{23}	J_{34}	J_{45a}	J_{45e}	J_{5a5e}	其他
β-木糖	8.5	8.5	10	4.3	10.4	
α-D-木糖四乙酸酯			11.0	5.4	11.2	
β-D-木糖四乙酸酯			8.6	4.7	11.8	
β-D-木糖-1-硫缩醛吡喃糖全乙酰化物	7.5	7.5	8.3	4.7	11.8	
β-来苏糖	3			5	10	
α-D-来苏糖四乙酸酯			8.6	4.3	11.6	
β-D-来苏糖四乙酸酯			5.3	3.1	12.4	
α-阿拉伯糖	9.9	3.6				
β-阿拉伯糖		3.4				
α-D-阿拉伯糖四乙酸酯			3.5	1.8	13.0	
β-D-阿拉伯糖四乙酸酯			1.8	1.2	13.2	
α-L-阿拉伯糖-1-硫缩醛吡喃糖全乙酰化物	8.0	3.3	2.3	4.7	12.5	
β-核糖	3.1	3.0	10			
α-D-核糖四乙酸酯			9.1	4.6	11.2	
β-D-核糖-1-硫缩醛吡喃糖全乙醛化物	3.0	3.0	7.5	4.7	11.8	
β-D-核糖四乙酸酯			3.3	5.8	12.4	$J_{13}=0.1$; $J_{15e}=0.2$ $J_{15a}=0.1$; $J_{14}=0.1$ $J_{24}=0.8$; $J_{35e}=0.45$
2,3,4-三苯甲酰基-β-D-核吡喃糖氟化物			1.9	1.35	1.35	
2,3,4-三苯甲酰基-β-D-核吡喃糖氯化物	3.9	3.9	1.9	1.7	14.0	
2,3,4-三苯甲酰基-β-D-核吡喃糖溴化物	3.9	3.9	1.5	1.4	13.8	
2,3,4-三苯甲酰基-β-D-核吡喃糖碘化物	4.0	4.0	1.6	1.5	13.4	
2,3,4-三苯甲酰基-β-D-核吡喃糖甲基甙	3.8	3.8	2.1	2.8	13.0	
2,3,4-三苯甲酰基-β-D-核吡喃糖苄基醚	3.8	3.8	2.5	3.0	13.2	
2,3,4-三苯甲酰基-α-D-核吡喃糖氟化物	3.3	2.9	10.8	5.3	10.9	
2,3,4-三苯甲酰基-α-D-核吡喃糖氯化物	3.3	3.3	10.7	5.1	10.9	
2,3,4-三苯甲酰基-α-D-核吡喃糖溴化物	3.0	3.1	10.7	5.6	10.8	
α-D-核吡喃糖四苯甲酸酯	3.4	3.2	9.3	4.6	10.9	
β-D-核吡喃糖四苯甲酸酯	3.6	3.6	2.5	3.9	12.9	
2,3,4-三苯甲酰基-β-D-核吡喃糖氰化物	3.2	3.2	6.6	4.3	12.4	
2,3-脱水-β-D-核吡喃糖甲基甙	4					
2,3-脱水-β-L-核吡喃糖甲基甙	3.8					

二、五碳呋喃糖衍生物的¹H-NMR化学位移和偶合常数

表 11-17　五碳呋喃糖衍生物的¹H-NMR化学位移[29,30]

化合物＼原子	1-H	2-H	3-H	4-H	5-H
1,2,3,5-四苯甲酰基-β-D-木呋喃糖	6.72	5.87	6.10	5.13	4.73
1-乙酰基-2,3,5-三苯甲酰基-β-D-木呋喃糖	6.45	5.70	5.93	5.03	4.68
2,3,5-三乙酰基-β-D-木呋喃糖氯化物	5.63	5.18	5.34	4.70	4.20,4.20
1,2,3,5-四苯甲酰基-α-D-木呋喃糖	6.98	5.98	6.27	5.12	4.65
1-乙酰基-2,3,5-三苯甲酰基-α-D-木呋喃糖	6.74	5.83	6.15	5.02	4.60
1,3,5-三苯甲酰基-2-甲磺酰基-α-D-木呋喃糖	6.83	5.63	6.05	5.02	4.57
1,3,5-三苯甲酰基-α-D-木呋喃糖	6.67	4.78	5.78	5.00	4.53
1,2,3,5-四苯甲酰基-β-D-来苏呋喃糖	6.90	5.80	6.28	4.97	4.78
1,2,3,5-四苯甲酰基-α-D-来苏呋喃糖	6.80	6.02	6.25	5.08	4.75
1,2,3,5-四苯甲酰基-β-D-阿拉伯呋喃糖	6.95	5.97	6.25	4.77	4.77
1,2,5-三苯甲酰基-3-乙酰基-β-D-阿拉伯呋喃糖	6.77	5.73	6.00	4.70	4.70
1,2,5-三苯甲酰基-3-甲磺酰基-β-D-阿拉伯呋喃糖	6.77	5.58	6.00	4.72	4.72
1,3,5-三苯甲酰基-β-D-阿拉伯呋喃糖	6.62	4.75	5.72	4.65	4.65
1,2,3,5-四苯甲酰基-α-D-阿拉伯呋喃糖	6.60	5.68	5.73	4.85	4.85
1-O-甲基-2,3,5-三苯甲酰基-α-D-阿拉伯呋喃糖	5.25	5.46	5.60	4.67	4.67
2,3,5-三苯甲酰基-α-D-阿拉伯呋喃糖氯化物	5.90	5.65	5.97	4.85	4.69,4.80
1,2,3,5-四苯甲酰基-α-D-核呋喃糖	6.98	5.77	5.97	4.96	4.75
1,3,5-三苯甲酰基-2-乙酰基-α-D-核呋喃糖	6.63	5.58	5.85	4.88	4.72
1,3,5-三苯甲酰基-2-甲磺酰基-α-D-核呋喃糖	6.65	5.47	5.82	4.87	4.68
1,3,5-三苯甲酰基-α-D-核呋喃糖	6.70	4.70	5.62	4.70	4.70
1,2,3,5-四苯甲酰基-β-D-核呋喃糖	6.73	6.05	6.08	5.0－5.42	5.0－5.42
1,3,5-三苯甲酰基-2-乙酰基-β-D-核呋喃糖	6.55	5.80	5.93	4.9～4.4	4.9～4.4
1-乙酰基-2,3,5-三苯甲酰基-β-D-核呋喃糖	6.47	5.82	5.97	4.9～4.4	4.9～4.4
1,2-二乙酰基-3,5-二苯甲酰基-β-D-核呋喃糖	6.30	5.58	5.82	4.63	4.63
1,3,5-三苯甲酰基-2-甲磺酰基-β-D-核呋喃糖	6.60	5.55	5.82	4.67	4.67
1,3,5-三苯甲酰基-β-D-核呋喃糖	6.47		5.63		
2,3,5-三苯甲酰基-β-D-核呋喃糖氯化物	5.96	5.46	5.57	4.90	4.57,4.74
2,3,5-三苯甲酰基-α-D-核呋喃糖氯化物	6.14	5.47	5.84	4.90	4.90,4.77
2-乙酰基-3,5-二苯甲酰基-β-D-核呋喃糖氯化物	5.79	5.76	5.62	4.77	4.52,4.71
2,5-二苯甲酰基-3-乙酰基-β-D-核呋喃糖氯化物	5.95	5.70	5.62	4.74	4.42,4.68
2,3-二苯甲酰基-5-乙酰基-β-D-核呋喃糖氯化物	6.04	5.81	5.75	4.82	4.25,4.61

表 11-18　五碳呋喃糖衍生物的¹H-NMR偶合常数(J)[29,30]

化合物＼偶合常数	J_{12}	J_{23}	J_{34}	J_{45}	J_{55}
1,2,3,5-四苯甲酰基-β-D-来苏呋喃糖	4.6	5.5	4.3		
1-乙酰基-2,3,5-三苯甲酰基-β-D-木呋喃糖	<0.5	1.8	5.2		
2,3,5-三乙酰基-β-D-木呋喃糖氯化物	1.0	<0.5	5.5	5.3,7.1	11.4
1,3,5-三苯甲酰基-2-甲磺酰基-α-D-木呋喃糖	4.4	6.4	6.8		
1,2,3,5-四苯甲酰基-α-D-来苏呋喃糖	1.5	5.2	5.4		
1,3,5-三苯甲酰基-2-甲磺酰基-β-D-阿拉伯呋喃糖	4.5	7.2	5.1		
1-O-甲基-2,3,5-三苯甲酰基-α-D-阿拉伯呋喃糖	<0.5	1.6	4.9		
2,3,5-三苯甲酰基-α-D-阿拉伯呋喃糖氯化物	<0.5	1.0	3.5	3.0,6.5	12.1
1,3,5-三苯甲酰基-2-甲磺酰基-α-D-核呋喃糖	4.3	6.5	2.3		
1,3,5-三苯甲酰基-2-甲磺酰基-β-D-核呋喃糖	<0.5	4.6	7.0		
1,3,5-三苯甲酰基-β-D-核呋喃糖	<0.5	1.8	5.2		
2,3,5-三苯甲酰基-β-D-核呋喃糖氯化物	<0.5	4.9	6.2	3.9,5.2	11.9
2,3,5-三苯甲酰基-α-D-核呋喃糖氯化物	3.5	6.9	2.5	3.2,3.8	12.3
2-乙酰基-3,5-二苯甲酰基-β-D-核呋喃糖氯化物	<0.5	4.7	6.7	3.8,5.6	12.5
2,5-二苯甲酰基-3-乙酰基-β-D-核呋喃糖氯化物	<0.5	5.0	5.0	4.5,5.4	12.4
2,3-二苯甲酰基-5-乙酰基-β-D-核呋喃糖氯化物	<0.5	4.9	4.9	3.6,5.3	12.1

三、六碳吡喃糖衍生物的^{1}H-NMR 化学位移和偶合常数

表 11-19　六碳吡喃糖衍生物的^{1}H-NMR 化学位移[31~36]

化合物 \ 质子	1-H	2-H	3-H	4-H	5-H	6-H
α-D-葡萄糖	5.28					
β-D-葡萄糖	4.70					
2-氨基-2-去氧-α-D-葡萄糖盐酸盐	5.46					
2-氨基-2-去氧-β-D-葡萄糖盐酸盐	4.96					
2-乙酰胺基-2-去氧-α-D-葡萄糖	5.18					
2-乙酰胺基-2-去氧-β-D-葡萄糖	4.70					
4-乙酰胺基-4-去氧-2,3,6-三乙酰基-β-L-吡喃葡萄糖甲基甙	4.47	4.95	5.22	4.20	3.78	4.28
3-乙酰胺基-3-去氧-2,4,6-三乙酰基-α-D-吡喃葡萄糖甲基甙	4.17	4.9	4.9	4.9	4.00	4.22
2-乙酰胺基-2-去氧-3,4,6-三乙酰基-α-D-吡喃葡萄糖甲基甙	4.75	4.30	5.25	5.08	3.93	4.20
2-乙酰胺基-2-去氧-3,4,6-三乙酰基-β-D-吡喃葡萄糖甲基甙	4.65	3.92	5.33	5.08	3.75	4.25
4-乙酰胺基-4-去氧-2,3,6-三乙酰基-α-L-吡喃葡萄糖甲基甙	5.02	5.20	5.37	4.27	3.96	4.27
4-乙酰胺基-4-去氧-2,3,6-三乙酰基-α-D-吡喃葡萄糖甲基甙	5.00	5.00	5.30	4.18	3.90	4.22
4-乙酰胺基-4-去氧-1,2,3,6-四乙酰基-β-L-吡喃葡萄糖	5.73	5.23	5.23	4.25	3.77	4.23
4,6-O-亚苄基-α-D-吡喃葡萄糖甲基甙	5.05	3.6~4.6	3.6~4.6	3.6~4.6	3.6~4.6	3.6~4.6
4,6-O-亚苄基-α-D-吡喃葡萄糖甲基甙-d_2	4.65	3.2~4.2	3.2~4.2	3.2~4.2	3.2~4.2	3.2~4.2
2,3-二乙酰基-4,6-O-亚苄基-α-D-吡喃葡萄糖甲基甙	5.14	5.23	5.97	3.6~4.5	3.6~4.5	3.6~4.5
2,3-二苯甲酰基-4,6-O-亚苄基-α-D-吡喃葡萄糖甲基甙	5.28	5.48	6.29	3.4~4.5	3.4~4.5	3.4~4.5
3-苯甲酰基-4,6-O-亚苄基-2-对甲苯磺酰基-α-D-吡喃葡萄糖甲基甙	5.04	4.68	5.83	3.5~4.5	3.5~4.5	3.5~4.5
4,6-O-亚苄基-2,3-二对甲苯磺酰基-α-D-吡喃葡萄糖甲基甙	5.23	4.92	5.52	3.4~4.5	3.4~4.5	3.4~4.5
2-乙酰基-4,6-O-硝基亚苄基-α-D-吡喃葡萄糖甲基甙-3-硝基物	5.06	4.90	5.72	3.6~4.5	3.6~4.5	3.6~4.5
4,6-O-亚苄基-2,3-二甲氧基-α-D-吡喃葡萄糖甲基甙	4.82	3.14~4.18	3.14~4.38	3.14~4.38	3.14~4.38	3.14~4.38
2-乙酰胺基-3-乙酰基-4,6-O-亚苄基-2-去氧-α-D-吡喃葡萄糖甲基甙	4.73	4.38	5.34	3.5~4.2	3.5~4.2	3.5~4.2
α-D-吡喃葡萄糖甲基甙-2,3-二磺酸钡盐	5.15	4.34	4.5	3.5~4.0	3.5~4.0	3.5~4.0
4,6-O-亚苄基-α-D-吡喃葡萄糖甲基甙-2,3-二磺酸钠盐	5.34	4.58	4.8	3.6~4.4	3.6~4.4	3.6~4.4
α-D-吡喃葡萄糖甲基甙-4,6-二磺酸钡盐	4.83	3.70	3.8~4.6	3.8~4.6	3.8~4.6	3.8~4.6
2,3-O-二苄基-α-D-吡喃葡萄糖甲基甙-4,6-二磺酸钡盐		3.62				
1-巯基-β-D-吡喃葡萄糖五乙酸酯	5.38	5.03	5.37	5.06	4.02	4.05;4.26
α-D-吡喃葡萄糖五乙酸酯	6.12	4.86	5.17	4.89	3.92	3.83,4.15
2,3,4,6-四乙酰基-α-D-吡喃葡萄糖甲基甙	4.86	4.74	5.29	4.92	3.88	3.97,4.17
β-D-吡喃葡萄糖五乙酸酯	5.63	4.9~5.2	4.9~5.2	4.9~5.2	3.94	4.09;4.28
2,3,4,6-四乙酰基-β-D-吡喃葡萄糖甲基甙	4.35	4.7~5.1	4.7~5.1	4.7~5.1	3.55	4.02,4.22
1,3,4,6-四乙酰基-2-(N-乙酰基乙酰胺基)-2-去氧-β-D-吡喃葡萄糖	6.60	3.90	5.92	5.13	3.9	

续表

化合物 \ 质子	1-H	2-H	3-H	4-H	5-H	6-H
1,3,4,6-四乙酰基-2-(*N*-乙酰基乙酰胺基)-2-去氧-α-D-吡喃葡萄糖	6.25	4.66	6.11	5.10	4.1	
1,3,4,6-四乙酰基-2-(*N*-乙酰基苯甲酰胺基)-2-去氧-β-D-吡喃葡萄糖	6.55	4.23	5.91	5.07	3.9	
1,3,4,5-四乙酰基-2-(*N*-乙酰基苯甲酰胺基)-2-去氧-α-D-吡喃葡萄糖	6.40	5.12	6.02	5.10	4.2	
2-乙酰胺基-1,3,4,6-四乙酰基-β-D-吡喃葡萄糖	5.77	4.44	5.2	5.1	3.9	
2-乙酰胺基-1,3,4,6-四乙酰基-2-去氧-α-D-吡喃葡萄糖	6.20	4.46	5.2	5.2	4.0	
α-D-半乳糖	5.29					
β-D-半乳糖	4.63					
2-乙酰胺基-2-去氧-α-D-半乳糖	5.28					
2-乙酰胺基-2-去氧-β-D-半乳糖	4.69					
2-氨基-2-去氧-α-D-半乳糖盐酸盐	5.48					
2-氨基-2-去氧-β-D-半乳糖盐酸盐	4.89					
1-巯基-β-D-吡喃半乳糖五乙酸酯	5.45	5.67	5.27	5.50	3.72	4.03;4.17
α-D-吡喃半乳糖甲基甙-2,3-二磺酸钡盐	5.17	4.55	4.38	3.6~4.0	3.6~4.0	3.6~4.0
β-D-吡喃半乳糖甲基甙-2,3-二磺酸钡盐	4.3~4.6	4.3~4.6	4.3~4.6	4.3~4.6	3.74	3.74
4,6-*O*-亚苄基-α-D-吡喃半乳糖甲基甙-2,3-二磺酸钡盐	5.33	4.8	4.8	4.8	3.95	4.24
4,6-*O*-亚苄基-β-D-吡喃半乳糖甲基甙-2,3-二磺酸钡盐	4.7m	4.7m	4.7m	4.7m	3.80	4.26
L-D-吡喃半乳糖甲基甙-2,6-二磺酸钡盐	5.14	4.55	3.85	4.0~4.2	4.0~4.2	3.5
β-D-吡喃半乳糖苄基甙-2,6-二磺酸钡盐	4.6	4.40	3.84	4.07	3.93	4.24
α-D-吡喃半乳糖甲基甙-4-磺酸钡盐	4.88	3.6~4.2	3.6~4.2	4.73	3.6~4.2	3.6~4.2
β-D-吡喃半乳糖甲基甙-4-磺酸钡盐	4.37					
α-D-甘露糖	5.20					
β-D-甘露糖	4.92					
2-乙酰胺基-2-去氧-α-D-甘露糖	5.11					
2-乙酰胺基-2-去氧-β-D-甘露糖	5.01					
2-氨基-2-去氧-α-D-甘露糖盐酸盐	5.4					
2-氨基-2-去氧-β-D-甘露糖盐酸盐	5.22					
4,6-*O*-亚苄基-α-D-吡喃甘露糖甲基甙	4.65	3.6~4.4	3.6~4.4	3.6~4.4	3.6~4.4	3.6~4.4
2,3-乙酰基-4,6-*O*-亚苄基-α-D-吡喃甘露糖甲基甙	4.66	5.3~5.5	5.3~5.5	4.0~4.4	4.0~4.4	4.0~4.4
2,3-二苯甲酰-4,6-亚苄基-α-D-吡喃甘露糖甲基甙	4.91	5.7~6.0	5.7~6.0	3.4~4.7	3.4~4.7	3.4~4.7
4,6-*O*-亚苄基-2,3-二对甲苯磺酰基吡喃甘露糖甲基甙	5.17	5.38	5.15	3.6~4.5	3.6~4.5	3.6~4.5
4,6-*O*-亚苄基-2,3-对硝基苯磺酰基-α-D-吡喃甘露糖甲基甙	5.08	4.97	4.76	3.6~4.3	3.6~4.3	3.6~4.3
2,3-脱水-4,6-*O*-亚苄基-α-D-吡喃甘露糖甲基甙	4.86	3.44	3.12	4.23	3.75	3.64
3-乙酰胺基-3-去氧-2,4,6-三乙酰基-α-D-吡喃甘露糖甲基甙	4.77	5.08	4.42	4.92	3.93	4.22
α-D-吡喃甘露糖五乙酸酯	5.81	5.0~5.23	5.0~5.23	5.0~5.23	3.94	4.20,3.97
2,3,4,6-四乙酰基-α-D-吡喃甘露糖甲基甙	4.60	5.0~5.3	5.0~5.3	5.0~5.3	3.85	4.16,4.01
β-D-吡喃甘露糖五乙酸酯	5.75	5.33	5.07	5.12	3.70	4.22,4.04
3-乙酸胺基-3-去氧-4,6-*O*-亚苄基-α-D-吡喃阿洛糖甲基甙	4.68	3.3~4.4	4.86	3.3~4.4	3.3~4.4	3.3~4.4
3-乙酰胺基-3-去氧-4,6-*O*-亚苄基-α-D-吡喃阿洛糖甲基甙-d_2	4.99	3.6~4.6	5.43	3.6~4.6	3.6~4.6	3.6~4.6

续表

化合物＼质子	1-H	2-H	3-H	4-H	5-H	6-H
3-乙酰胺基-3-去氧-2-乙酰基-4,6-*O*-亚苄基-*α*-D-吡喃阿洛糖甲基甙-d	5.02	5.23	5.49	3.6～4.5	3.6～4.5	3.6～4.5
β-D-吡喃阿洛糖五乙酸酯	6.05	5.02	5.75	5.05	4.26	
2,3-脱水-4,6-*O*-亚苄基-*α*-D-吡喃阿洛糖甲基甙	4.88	3.3～3.6	3.3～3.6	4.3	3.6～4.0	3.6～4.0
4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.68	3.8～4.5	3.8～4.5	3.8～4.5	3.8～4.5	3.8～4.5
2,3-二乙酰基-4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.59	5.03	5.24	3.5～4.5	3.5～4.5	3.5～4.5
2,3-二苯甲酰基-4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.82	5.45	5.75	3.7～4.7	3.7～4.7	3.7～4.7
4,6-*O*-亚苄基-2-*O*-甲基-*α*-D-吡喃阿卓糖甲基甙	4.69	3.46	3.6～4.4	3.6～4.4	3.6～4.4	3.6～4.4
4,6-*O*-亚苄基-2,3-*O*-二甲基-*α*-D-吡喃阿卓糖甲基甙	4.78	3.62	3.85	3.7～4.6	3.7～4.6	3.7～4.6
2-氨基-2-去氧-4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.51	3.24	3.5～4.4	3.5～4.4	3.5～4.4	3.5～4.4
3-氨基-3-去氧-4,6-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.67	3.7～4.4	3.28	3.7～4.4	3.7～4.4	3.7～4.4
3-乙酰胺基-3-去氧-4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.65	3.6～4.4	4.72	3.6～4.4	3.6～4.4	3.6～4.4
3-乙酰胺基-3-去氧-2-乙酰基-4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.88	5.38	5.11	3.6～4.6	3.6～4.6	3.6～4.6
3-苯甲酰胺基-3-去氧-4,6-*O*-亚苄基-*α*-D-吡喃阿卓糖甲基甙	4.73	3.6～4.5	5.14	3.6～4.5	3.6～4.5	3.6～4.5
2-乙酰基-4,6-*O*-亚苄基-3-去氧-3-(2,4-二硝基苯胺基)-*α*-D-吡喃阿卓糖甲基甙	4.82	5.10	3.7～4.6	3.7～4.6	3.7～4.6	3.7～4.6
4,6-*O*-亚苄基-3-去氧-3-(2,4-二硝基苯胺基)-2-*O*-甲基-*α*-D-吡喃阿卓糖甲基甙	5.02	3.77	3.8～4.8	3.8～4.8	3.8～4.8	3.8～4.8
α-D-吡喃伊杜糖五乙酸酯	5.98	4.81	5.01	4.91	4.53	4.15

表 11-20　六碳吡喃糖衍生物的^{1}H-NMR 偶合常数[31～36]

化合物＼偶合常数	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
4,6-*O*-亚苄基-*α*-D-吡喃葡萄糖甲基甙	3.5						
4,6-*O*-亚苄基-*α*-D-吡喃葡萄糖甲基甙-d_2	3.6						
2,3-二乙酰基-4,6-*O*-亚苄基-*α*-D-吡喃葡萄糖甲基甙	3.6	9.8	8.5				
3-苯甲酰基-4,6-*O*-亚苄基-2-对甲苯磺酰基-*α*-D-吡喃葡萄糖甲基甙	3.7	9.6	9.5				
4,6-*O*-亚苄基-2,3-二对甲苯磺酰基-*α*-D-吡喃葡萄糖甲基甙	3.6	9.4	9.0				
2-乙酰胺基-2-去氧-3-乙酰基-4,6-*O*-亚苄基-*α*-D-吡喃葡萄糖甲基甙	3.5	9.2	9.2				
α-D-吡喃葡萄糖甲基甙-2,3-二磺酸钡盐	3.5	10.0					
1-巯基-*β*-D-吡喃葡萄糖五乙酸酯	10.6	9.5	9.5	10.1	5.4		13.2
α-D-吡喃葡萄糖五乙酸酯	3.6	10.0	9.3	9.3	4.7	2.3	12.2
1-*O*-甲基-2,3,4,6-四乙酰基-*α*-D-吡喃葡萄糖	3.7	9.2	9.3	9.3	4.7	2.3	12.2
β-D-吡喃葡萄糖五乙酸酯	8.0	10.2		9.5	4.6	2.0	12.5
1-*O*-甲基-2,3,4,6-四乙酰基-*β*-D-吡喃葡萄糖	7.5				4.7	2.5	12.5
1,3,4,6-四乙酰基-2-(*N*-乙酰乙酰胺基)-2-去氧-*β*-D-吡喃葡萄糖	8.3	10.3	9.0	10.2	4.7	2.0	
1,3,4,6-四乙酰基-2-(*N*-乙酰乙酰胺基)-2-去氧-*α*-D-吡喃葡萄糖	3.5	10.3	9.0	9.0			
1,3,4,6-四乙酰基-2-(*N*-乙酰苯甲酰胺基)-2-去氧-*β*-D-吡喃葡萄糖	8.5	10.9	9.0	10.0	4.5	1.9	
1,3,4,5-四乙酰基-2-(*N*-乙酰苯甲酰基)-2-去氧-*α*-D-吡喃葡萄糖	3.5	11.0	9.0	9.0			
2-乙酰胺基-1,3,4,6-四乙酰基-*β*-D-吡喃葡萄糖	8.8						
2-乙酰胺基-1,3,4,6-四乙酰基-2-去氧-*α*-D-吡喃葡萄糖	3.5						
1-巯基-*β*-D-吡喃半乳糖五乙酸酯	10.0	9.4	3.4	1.2	6.7	6.0	11.2
α-D-吡喃半乳糖甲基甙-2,6-二磺酸钡盐	3.5	10.0					

续表

化合物 \ 偶合常数	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
β-D-吡喃半乳糖苄基苷-2,6-二硫酸酯钠	7.7	9.3	3.0	0.5	6.3		
β-D-吡喃半乳糖苄基苷-4-硫酸酯钠	7.0						
4,6-O-亚苄基-α-D-吡喃甘露糖甲基苷	0.6						
2,3-二乙酰基-4,6-O-亚苄基-α-D-吡喃甘露糖甲基苷	1.2						
4,6-O-亚苄基-2,3-二对甲苯磺酰基吡喃甘露糖甲基苷	1.7	3.0	9.4				
2,3-脱水-4,6-O-亚苄基-α-D-吡喃甘露糖甲基苷	0	4.0	0	5			
α-D-吡喃甘露糖五乙酸酯	1.8				4.6	2.5	12.5
1-O-甲基-2,3,4,6-四乙酰基-α-D-吡喃甘露糖	1.6			9.2	5.2	2.7	12.1
β-D-吡喃甘露糖五乙酸酯	1.4	3.3	9.5	9.5	5.0	2.5	12.2
1-O-甲基-2,3,4,6-乙酰基-β-D-吡喃甘露糖	1.2	3.4	10	10	5.0	2.7	12.5
3-乙酰胺基-4,6-O-亚苄基-3-去氧-α-D-吡喃阿卓糖甲基苷	3.2						
3-乙酰胺基-4,6-O-亚苄基-3-去氧-α-D-吡喃阿卓糖甲基苷-d_2	3.4	3.9	3.9				
3-乙酰胺基-2-乙酰基-3-去氧-4,6-O-亚苄基-α-D-吡喃阿卓糖甲基苷	3.5	4.4	4.2				
β-D-吡喃阿卓糖五乙酸酯	8.6	2.9	2.9				
2,3-脱水-4,6-O-亚苄基-α-D-吡喃阿卓糖甲基苷	2.5	4.5	4.5	10			
4,6-O-亚苄基-α-D-吡喃阿卓糖甲基苷	<0.6						
2,3-二乙酰基-4,6-亚苄基-α-D-吡喃阿卓糖甲基苷	0.9	2.9	2.9				
4,6-O-亚苄基-2-O-甲基-α-D-吡喃阿卓糖甲基苷	1.0	3.0					
4,6-O-亚苄基-2,3-O-二甲基-α-D-吡喃阿卓糖甲基苷	0.8	2.8	2.8				
2-氨基-4,6-O-亚苄基-2-去氧-α-D-吡喃阿卓糖甲基苷	0.8	2.5					
3-乙酰胺基-2-乙酰基-4,6-O-亚苄基-3-去氧-α-D-吡喃阿卓糖甲基苷	1.0	2.7					
2-乙酰基-4,6-O-亚苄基-3-去氧-3-(2,4-二硝基苯胺基)-α-D-吡喃阿卓糖甲基苷	1.1	2.5					
α-D-吡喃伊杜糖五乙酸酯	2.1	3.6	3.5	2.1	6.0		

四、几种低聚糖苷的^{1}H-NMR化学位移[91]

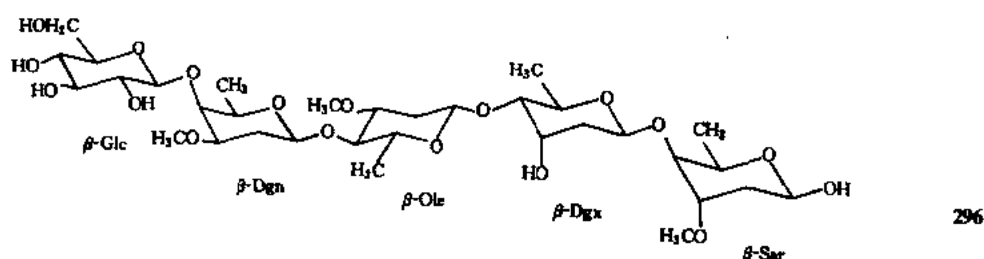
表 11-21 低聚糖 296~300 中 β-葡萄糖，β-2-脱氧毛地黄糖，β-齐墩果糖和β-毛地黄毒糖的^{1}H-NMR化学位移和偶合常数[91]

六碳糖质子		1	2		3	4	5	6_A	6_B
β-Glc	多重性	d	dd		t	t	ddd	dd	dd
	J(296)	7.7	9.2		9.0	9.6	1.8	11.8	5.7
	δ_H(296)	4.566	3.213		3.355	3.264	3.256	3.863	3.648
	δ_H(297)	4.558	3.208		3.35	3.28	3.24	3.87	3.666
	δ_H(298)	4.556	3.211		3.35	3.28	3.27	3.89	3.65
2-去氧六碳糖质子		1	2_{eq}	2_{ax}	3	4	5	6	OCH_3
β-Dg	多重性	dd	ddd	dddd	ddd	d(d)	dq	d	s
	J(296)	2.2/9.9	12.1	12.1	4.4	2.8	1.1	6.4	—
	δ_H(296)	4.674	1.754	1.996	3.449	3.989	3.504	1.304	3.395
	δ_H(297)	4.572	1.80	2.01	3.44	3.989	3.525	1.295	3.397
	δ_H(298)	4.566	1.741	1.996	3.454	3.987	3.524	1.295	3.397
	δ_H(299)	4.545	1.677	1.902	3.393	3.866	3.474	1.271	3.367
β-Ol	多重性	dd	ddd	ddd	ddd	t	dq	d	s
	J(296)	2.0/9.7	11.6	12.6	5.3	9.0	8.8	6.1	—
	J(300)	1.9/9.9	11.5	12.6	4.6	8.9	9.4	6.1	—
	δ_H(296)	4.631	1.459	2.325	3.395	3.166	3.358	1.285	3.397
	δ_H(300)	4.593	1.349	2.326	3.472	2.960	3.208	1.273	3.413
β-Dt	多重性	dd	ddd	ddd	ddd	dd	dq	d	—
	J(296)	2.2/9.9	3.1	13.8	3.5	2.8	9.6	6.3	—
	δ_H(296)	4.852	1.684	2.060	4.222	3.258	3.604	1.219	—

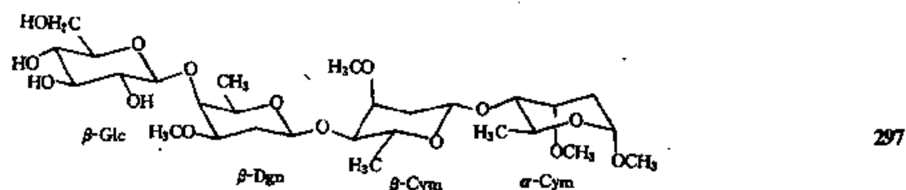
表 11-22 低聚糖 296～300 中磁麻糖和箭毒羊角拗糖的^{1}H-NMR 化学位移和偶合常数[91]

2-去氧六碳糖质子		1(α-OMe)	2_{ax}	2_{eq}	3	4	5	6	OCH_3
β-Sar	多重性	dd	ddd	dddd	ddd	dd	dq	d	s
	J(296)①	2.2/9.9	3.1	13.6	3.3	3.0	1.5	6.4	—
	δ_H(296)	4.848	1.680	1.822	3.779	3.351	3.879	1.181	3.366
α-Sar	多重性	br dd	ddddd	dt	ddd	br s	dq	d	s
	J(300)	3.8/1.3	3.3	15.0	3.3	3.2	1.3	6.7	—
	δ_H(298)	4.607(3.279)	1.824	1.930	3.66	3.43	4.092	1.149	3.348
	δ_H(299)	4.608(3.279)	1.793	1.956	3.680	3.448	4.093	1.148	3.348
	δ_H(300)	4.607(3.279)	1.784	1.954	3.677	3.448	4.090	1.148	3.347
β-Cym	多重性	dd	ddd	ddd	ddd	dd	dq	d	s
	J(299)	1.8/9.9	2.7	13.9	3.2	2.8	9.6	6.2	—
	J(300)	1.9/9.9	2.4	13.9	3.1	2.8	9.6	6.4	—
	δ_H(297)	4.782	1.56	2.235	3.83	3.29	3.84	1.213	3.411
	δ_H(298)	4.852	1.558	2.231	3.84	3.29	3.84	1.211	3.413
	δ_H(299)	4.791	1.566	2.203	3.869	3.278	3.815	1.207	3.431
	δ_H(300)	4.787	1.575	2.185	3.858	3.213	3.814	1.212	3.429
α-Cym	多重性	br d	ddd	ddd	ddd	dd	dq	d	—
	J(297)	≈4	2.8	◇	3.3	2.8	◇	6.6	—
	δ_H(297)	4.599(3.361)	1.66	1.80	3.771	3.29	3.84	1.197	3.408

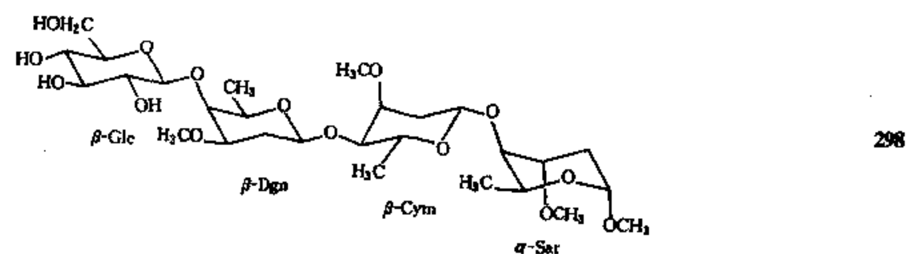
① 括号内为化合物编号。



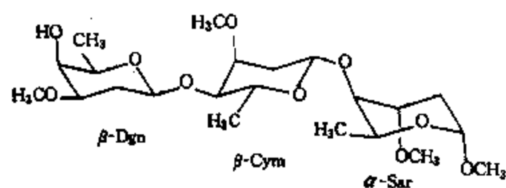
296



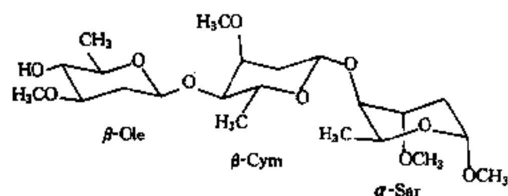
297



298



299



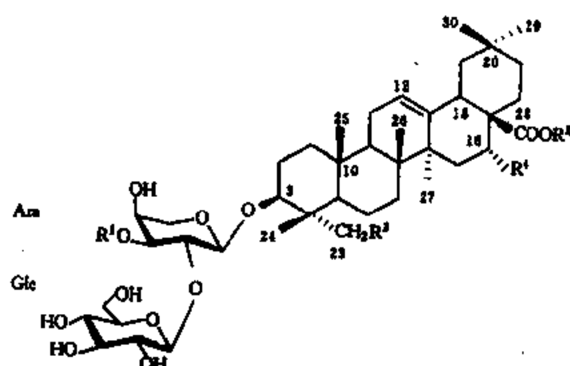
300

表 11-23 几种多糖苷糖体部分的 ^{1}H-NMR 化学位移[92]

质子 \ 化合物	301	302	303	304
C-3				
Ara 1	4.78d(6.6)	4.78d(6.8)	4.75d(7.0)	4.76d(6.9)
2	4.72t(7,8)	4.71t(7,8)	4.72t(7,8)	4.72t(7,8)
3	4.34	4.32	4.28	4.27
4	4.54brs	4.53brs	4.45brs	4.46brs
5A	3.72d(11)	3.72d(11)	3.67d(10)	3.68
5B	4.26	4.26	4.16	4.18
Glc'(1→2)Ara				
1	5.53d(8.2)	5.51d(7.8)	5.52d(7.9)	5.50d(7.7)
2	3.97	3.95t(8,9)	4.03t(8)	4.02t(8)
3	4.15	4.13	4.21	4.18
4	4.05t(9)	4.02	4.13	4.14
5	3.77m	3.76m	3.72m	3.72m
6A	4.24	4.22	4.29dd(11,3)	4.28
6B	4.40brd(12)	4.40brd(10)	4.37dd(11,3)	4.38dd(12,3)
Glc(1→3)Ara				
1	5.27d(7.8)	5.27d(7.9)	5.26d(7.8)	5.26d(8.0)
2	4.00t(8)	4.00	3.98t(8)	3.98t(8,9)
3	4.20	4.19	4.22t(9)	4.22t(9)
4	4.27	4.26	4.27t(9)	4.27t(9)
5	3.92	3.91	3.87m	3.89m
6A	4.46	4.47	4.41dd(11,3)	4.42dd(11,3)
6B	4.52	4.47	4.48dd(12,4)	4.48dd(11,3)
Gal(1→4)Glc				
1	5.13d(7.7)	5.13d(7.9)	5.11d(7.6)	5.13d(7.7)
2	4.59t(8,9)	4.58t(8,9)	4.66t(8)	4.66t(8)
3	4.20	4.20	4.18	4.19
4	4.68brs	4.68brs	4.67brs	4.67brs
5	4.19	4.19	4.17	4.16
6A	4.33	4.32	4.33	4.33dd(12,4)
6B	4.44	4.43dd(12,3)	4.46d(12)	4.44
Xyl(1→3)Gal				
1	5.24d(7.5)	5.23d(7.5)	5.23d(7.6)	5.23d(7.7)
2	3.97t(8)	3.97t(8,9)	3.99t(8,9)	3.99t(8,9)
3	4.10	4.10	4.15	4.15

续表

质子 \ 化合物	301	302	303	304
Xyl(1→3)Gal				
4	4.13	4.12	4.18	4.17
5A	3.70d(11)	3.70d(10)	3.67d(11)	3.69
5B	4.32	4.31	4.30	4.30
C-28				
Glc″1	6.25d(8.2)	6.24d(8.2)		
2	4.10	4.04		
3	4.21	4.17		
4	4.24t(8)	4.16		
5	4.10	4.09		
6A	4.34	4.32		
6B	4.70d(10)	4.68d(12)		
Glc‴(1→6)Glc″				
1	4.99d(7.9)	4.97d(7.9)		
2	3.91t(8,9)	3.91t(8,9)		
3	4.13	4.11		
4	4.33	4.32		
5	3.73	3.71		
6A	4.12	4.12		
6B	4.27	4.27		
Rha(1→4)Glc‴				
1	5.85brs	5.83brs		
2	4.62brs	4.61brs		
3	4.48	4.47		
4	4.26t(8)	4.24		
5	4.85m	4.85m		
6	1.71d(6)	1.71d(6)		

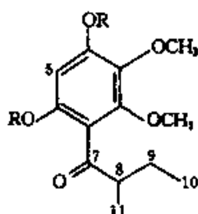


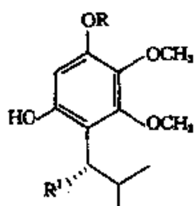
	R^1	R^2	R^3	R^4
301.	Xyl(1→3)Gal(1→4)Glc	Rha(1→4)Glc(1→6)Glc	H	H
302.	Xyl(1→3)Gal(1→4)Glc	H	H	H
303.	Xyl(1→3)Gal(1→4)Glc	Rha(1→4)Glc(1→6)Glc	H	OH
304.	Xyl(1→3)Gal(1→4)Glc	H	H	OH

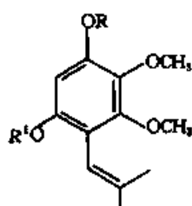
第五节　天然芳香化合物的¹H-NMR化学位移

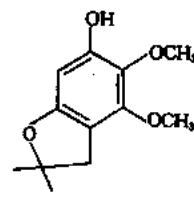
表 11-24　天然芳环化合物 305～313 的¹H-NMR 化学位移[37]

质子＼化合物	305	306	307	308	309	310	311	312	313
5-H	6.30s	6.72s	5.83s	6.08s	6.06s	6.09s	6.56s	6.41s	5.98s
7-H	—	—	4.39d	4.75d	4.46d	5.94qq	5.66qq	5.77qq	2.91s
8-H	3.72tq	3.48tq	2.04dqq	2.07dqq	2.04dqq	—	—	—	—
9-H	1.81dq	1.80dq	1.03d	1.07d	1.02d	1.95d	1.84d	1.88d	1.46s
	1.41dq	1.43dq							
10-H	0.92t	0.96t	0.89d	0.80d	0.84d	1.62d	1.56d	1.57d	1.46s
11-H	1.17d	1.15d	—	—		—	—	—	—
OCH_3	3.96s	3.89s	3.83s	3.86s	3.87s	3.89s	3.85s	3.90s	3.82s
	3.84s	3.85s	3.82s	3.83s	3.83s	3.84s	3.81s	3.80s	3.80s
	—	—	3.39s	3.77s	3.76s	3.79s	—	3.77s	—
	—	—	—	3.37s	—	—	—	—	—
$OCOCH_3$	—	2.33s	—	—	—	—	2.25s	2.24s	—
	—	2.20s	—	—	—	—	2.20s	—	—
OH	13.25s	—	8.19s	7.06s	8.52s	5.77s	—	—	5.76s









305. R＝H
306. R＝$COCH_3$

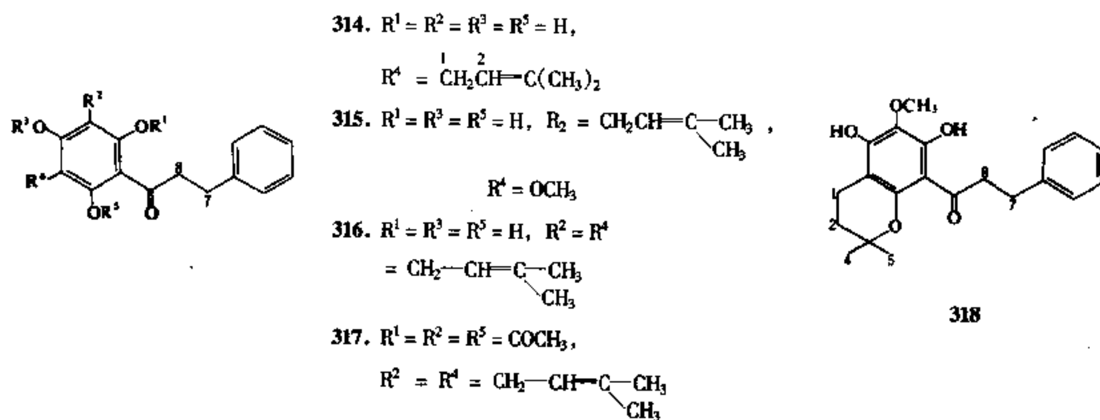
307. R＝H，R^1＝OCH_3
308. R＝CH_3，R^1＝OH
309. R＝CH_3，R^1＝OCH_3

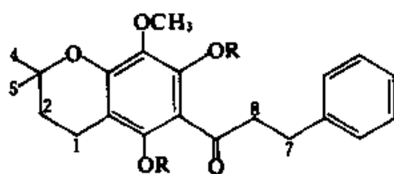
310. R＝CH_3，R^1＝H
311. R＝R^1＝$COCH_3$
312. R＝CH_3，R^1＝$COCH_3$

313

表 11-25　天然芳环化合物 314～321 的¹H-NMR 化学位移[38]

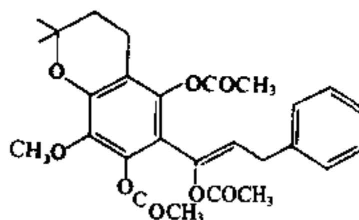
质子＼化合物	314	315	316	317	318	319	320	321
1-H	4.49bd	3.30bd	3.37bd	3.08bd	2.62t	2.64t	2.53t	2.52m
2-H	5.44bt	5.25bt	5.22bt	4.97bt	1.77t	1.81t	1.78t	—
4-H	1.79bs	1.76bs	1.83bs	1.66bs	1.34s	1.39s	1.37s	1.36s
5-H	1.79bs	1.64bs	1.77bs	1.66bs	1.34s	1.39s	1.37s	1.36s
7-H	3.02bt	3.01bt	3.01bt	2.95bt	3.02bt	3.03bt	2.99m	3.39d
8-H	3.40bt	3.44bt	3.39bt	3.06bt	3.40bt	3.41bt	2.99m	5.46t
OCH_3	—	3.71s	—	—	3.90s	3.82s	3.79s	3.79s
$OCOCH_3$	—	—	—	2.08s	—	—	2.15s	2.10s
	—	—	—	2.36s	—	—	2.17s	2.17s
OH	—	13.61s	—	—	13.96s	13.74s	—	—
	—	—	—	—	6.45s	6.62s	—	—





319. R = H

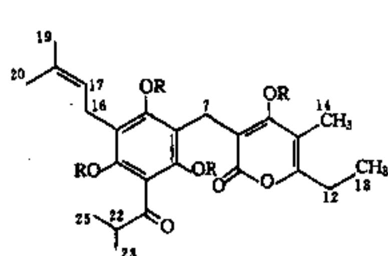
320. R = $COCH_3$

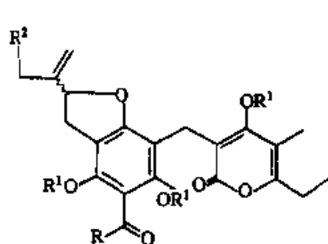


321

表 11-26 天然芳环化合物 322～329 的^{1}H-NMR 化学位移[39]

质子 \ 化合物	322	323	324	325	326	327	328	329
7-H	3.65bs	3.53bs	3.59bs	3.66dd	3.58bs	3.63bs	3.68bs	3.52bs
				3.54dd				
12-H	2.55q	2.56q	2.58q	2.55q	2.58q	2.57q	2.57q	2.56q
13-H	1.19t	1.24t	1.23t	1.23t	1.22t	1.22t	1.14t	1.23t
14-H	1.94s	1.75s	1.97s	1.78s	1.96s	1.96s	1.96s	1.76s
16-H	3.45bd	3.09bd	3.34dd	3.17dd	3.35dd	2.93dd	—	—
			3.02dd	2.88dd	3.02dd	2.68dd		
17-H	5.21bt	4.98bt	5.41dd	5.22dd	5.43dd	3.20dd	—	—
19-H	1.78bs	1.67bs	5.14bs	5.03bs	5.20bs	1.53s	—	—
			5.03bs	4.90bs	5.05bs	1.46s		
20-H	1.84bs	1.67bs	1.78bs	1.74bs	2.08bt	2.74s	3.90tq	2.93qq
22-H	3.94qq	2.93qq	2.73s	2.76tq	2.73	—	1.38m	1.11d
23-H	1.17d	1.13d	—	1.8m	—	—	0.91	—
25-H	1.17d	1.13d	—	—	—	—	—	—
OH	10.08bs	—	13.90s	—	13.89s	14.11s	16.2s	—
	—	—	10.38s	—	10.37s	10.59s	12.1s	—
	—	—	8.48s	—	8.47s	9.04s	10.9s	—





322. R = H

323. R = $COCH_3$

324. $R^1 = CH_3—CH(CH_3)—CH_2CH_2—$

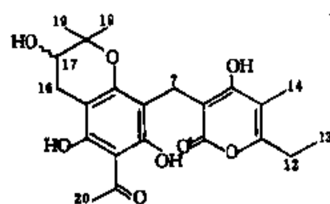
$R^1 = R^2 = H$

325. $R = CH_3—CH(CH_3)—CH_2—$

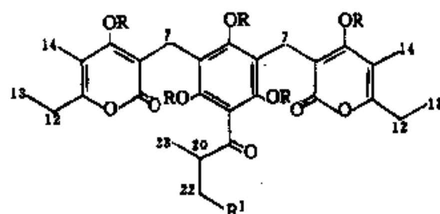
$R^1 = COCH_3, R^2 = H$

326. $R = CH_3, R^1 = H,$

$R^2 = CH_2—CH{=}C(CH_3)—CH_3$



327

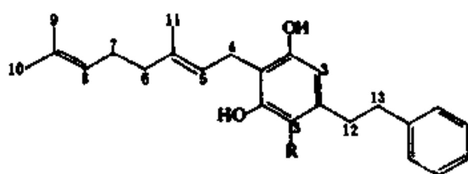


328. R = H, $R^1 = CH_3$

329. R = $COCH_3$, R^1 = H

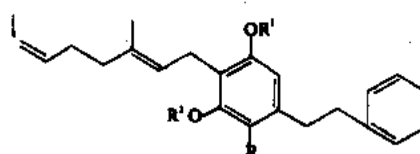
表 11-27 天然芳环化合物 330 ~ 335 的 ^{1}H-NMR 化学位移[40]

化合物 / 质子	330	331	332	333	334	335	化合物 / 质子	330	331	332	333	334	335
3-H	6.23s	6.26s	7.11s	6.60s	6.52s	6.58s	11-H	1.82bs	1.82bs	1.73bs	1.83bs	—	1.83bs
4-H	3.40bd	3.45bd	3.20bd	3.49bd	3.27bd	3.49bd	12-H	2.84m	3.13	7.06d	7.69d	3.14	7.68d
5-H	5.27bt	5.29bt	5.07bt	5.30bt	5.07bt	5.30bt	13-H	2.84m	2.83	6.98d	6.79d	2.84	6.78d
6-H	2.08bs	2.08bs	2.02bs	2.10m	1.64bs	2.79bd	苯环H	7.28m	7.31m	7.48bd	7.49bd	7.29m	7.49bd
7-H	2.08bs	2.08bs	2.02bs	2.10m	1.67bs	5.59d		7.20m	7.21m	7.35bt	7.37bt	7.20m	7.37bt
8-H	5.06bt	5.07bt	5.05bt	5.07bt	—	5.59d	—OC_2CH_3	—	3.96s	—	3.95s	3.97s	3.95s
9-H	1.59bs	1.60bs	1.59bs	1.60bs	—	1.34s	OH	5.01bs	5.91bs	—	5.95s	11.74s	11.98s
10-H	1.69bs	1.68bs	1.66bs	1.69bs	—	1.34s		—	12.1s	—	12.0s	—	—



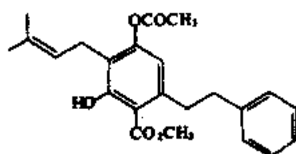
330. R = H

331. R = CO_2CH_3

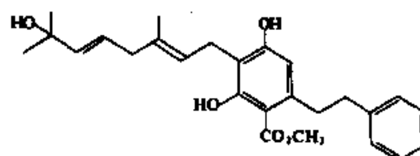


332. R = H, R^1 = $COCH_3$

333. R = CO_2CH_3, R^1 = H



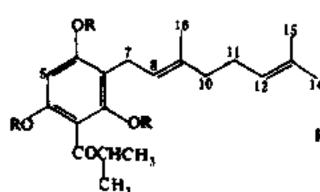
334



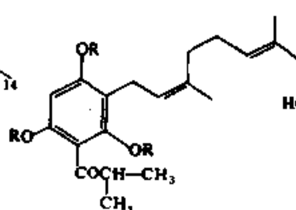
335

表 11-28 天然芳环化合物 336~341 的^{1}H-NMR 化学位移[41]

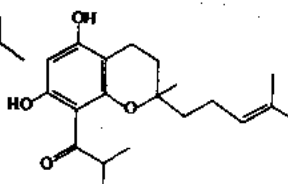
质子 \ 化合物	336	337	338	339	340	341
5-H	5.89s	7.02s	5.88s	7.01s	5.95s	5.93s
7-H	3.37bd	3.14bd	3.37bd	3.14bd	2.60t	2.58t
					2.59t	2.57t
8-H	5.06bt	5.02bt	5.18bt	5.02bt	2.08m	2.05t
10-H	2.08bs	2.12bs	2.26bt	2.2~2.35m	1.7~1.9m	2.07t
11-H	2.08bs	2.12bs	2.16bt	2.2~2.35m	1.7~1.9m	1.7~1.9m
12-H	5.26bt	5.13bt	5.24bt	5.05bt	5.11bs	1.7~1.9m
14-H	1.59bs	1.59bs	1.63bs	1.63bs	1.61bs	5.10bt
15-H	1.67bs	1.67bs	1.70bs	1.68bs	1.69bs	1.60bs
16-H	1.76bs	1.70bs	1.81bs	1.70bs	1.35s	1.68bs
$COCH_3$	—	2.28s	—	2.28s	13.89	1.30
	—	2.23s	—	2.23s	—	—
	—	2.22s	—	2.22s	—	—



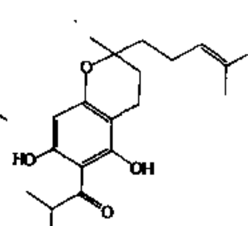
336. R = H
337. R = $COCH_3$



338. R = H
339. R = $COCH_3$



340

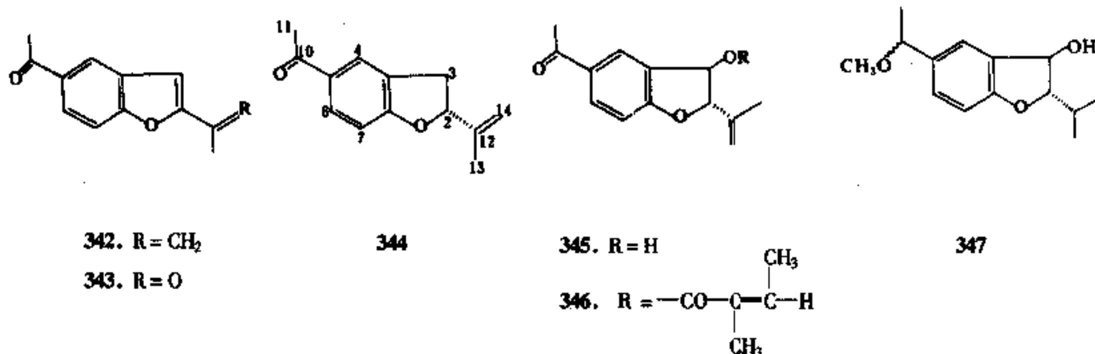


341

表 11-29 天然芳环化合物 342~347 的^{1}H-NMR 化学位移[42]①

质子 \ 化合物	342	343	344	345	346	347
2-H	—	—	5.29t(9)	5.05d(3.7)	5.00d(2.5)	5.09m
3-H	6.67s	7.57s	3.08m	4.97bs	6.17d(2.5)	4.88m
			3.36m	3.87bs		
4-H	8.17d(2)	8.35d(1.7)	7.84m	8.02d(2)	8.04d(2)	7.32m
6-H	7.93dd(2,8.7)	8.13dd(1.7,9)	7.84m	7.88dd(2,8.5)	7.93dd(2,8.5)	7.24dd(2,8.5)
7-H	7.43d(8.7)	7.62d(9)	6.81d(9)	6.88d(8.5)	6.89d(8.5)	6.84d(8.5)
10-H	—	—	—	—	—	4.40q(6.5)
11-H	2.22s	2.68s	2.53s	2.51s	2.47s	1.40d(6.5)
13-H	1.80s	2.63s	1.76bs	1.73s	1.71s	1.76s
14-H	5.23bs	—	5.09bs	4.93bs	4.90d(1)	5.09m
	5.83bs	—	5.18bs	5.08bs	5.03d(1)	4.88m

① 表中括号内的数值为 J 值。



342. R = CH_2
343. R = O

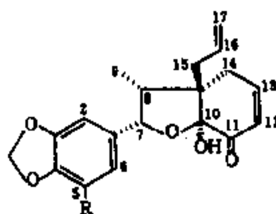
344

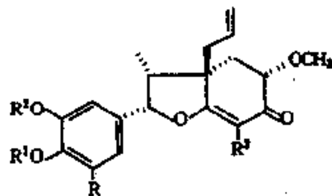
345. R = H
346. R = —CO—C(CH₃)=C(CH₃)—H

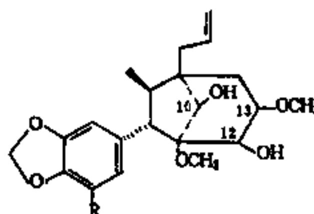
347

表 11-30 天然芳环化合物 348 ~ 354 的 ^{1}H-NMR 化学位移[43]

质子＼化合物	348	349	350	351	352	353	354
2-H	6.40bs	6.72bs	6.50	6.5 ~ 6.8	6.76	6.35	6.95
5-H	—	6.72bs	—	6.5 ~ 6.8	6.93	—	6.64
6-H	6.40bs	6.72bs	6.15	6.5 ~ 6.8	6.83	6.48	6.75
7-H	5.34d	5.38d(10)	5.82	5.75	5.89d(1.5)	1.9 ~ 2.8	3.25d(9)
8-H	2.84m	2.85dd(10,8)	2.6	2.6	2.6m	1.9 ~ 2.8	2.4 ~ 2.5m
9-H	0.70d	0.76d(8)	0.56	0.55	0.52d(7.5)	0.9	0.86d(7)
10-H	—	—	—	—	—	3.52	—
11-H	—	—	—	—	5.59s	—	—
12-H	6.24	6.22dd(10,3)	—	—	—	4.00	4.03d(6.5)
13-H	6.95	6.93ddd(10,5,3)	3.94	3.80	4.02dd(12,5)	3.70	3.62t(6.5)
14-H$_a$	2.06	2.01dd(13,5)	1.84	1.7 ~ 2.7	1.92t(12)	1.5 ~ 1.9	1.54dd(16,6)
14-H$_e$	2.49	2.45dt(13,3,3)	2.20	1.7 ~ 2.7	2.22dd(12,5)	1.5 ~ 1.9	1.86d(16)
15-H$_a$	2.1 ~ 2.4m	2.1 ~ 2.4m	2.4 ~ 2.7	1.7 ~ 2.7	2.56dd(14,7)	1.9 ~ 2.8	2.05dd(14,9)
15-H$_b$	2.1 ~ 2.4m	2.1 ~ 2.4m	2.4 ~ 2.7	1.7 ~ 2.7	2.69dd(14,7)	1.9 ~ 2.8	2.4 ~ 2.5m
16-H	5.4 ~ 5.8m	5.4 ~ 5.8m	5.7 ~ 6.1	5.5 ~ 5.9	5.9 ~ 6.1m	3.4 ~ 4.2	3.8 ~ 4.0m
17-H	4.8 ~ 5.2m	4.8 ~ 5.2m	5.2 ~ 5.4	4.9 ~ 5.3	5.3 ~ 5.4m	4.8 ~ 5.2	5.0 ~ 5.2m
—O—CH_2—O	5.93s	5.96s	6.00s	5.92s	—	5.90	5.90
11-OCH_3	—	—	3.80s	3.80s	—	3.20s	3.22s
5-OCH_3	—	—	3.62s	3.62s	3.62s	3.40s	3.40s







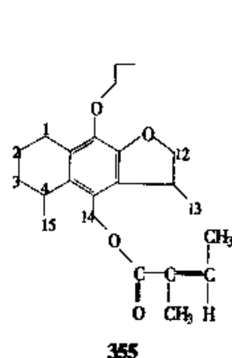
348. R = OCH_3
349. R = H

350. R = R³ = OCH_3, R¹ + R² = CH_2
351. R = H, R¹ + R² = CH_2, R³ = OCH_3
352. R = R³ = H, R¹ = R² = CH_3

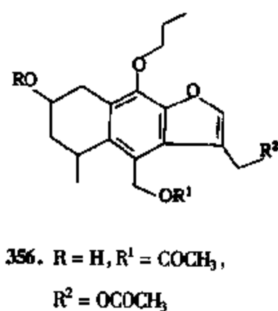
353. R = OCH_3
354. R = H

表 11-31　天然芳环化合物 355～360 的^{1}H-NMR 化学位移[44]

质子 \ 化合物	355	356	357	358	359	360
1-$H_α$	2.85bdd(17)	3.27ddd	3.27ddd	3.32ddd	2.88ddd	2.97ddd
1-$H_β$	2.60ddd(17)	2.51dd	2.51dd	2.60dd	2.78ddd	2.75dd
2-H	1.8～1.86m	4.35dddd	4.35dddd	5.38m	1.9～2.01m	1.91～2.01m
3-$H_α$	—	2.10dddd	2.10dddd	2.11dddd	5.12m	4.09ddd
3-$H_β$	—	1.86ddd	1.86ddd	1.92ddd	—	—
4-H	3.46ddq	3.65ddq	3.65ddq	3.66ddq	3.47dq	3.50dq
12-H	7.30q	7.64bs	7.31q	7.65bs	7.32q	7.31q
13-H	2.30d	5.22s	2.31d	5.23s	2.39d	2.31d
14-H	5.57d(12)	5.53d	5.54d(12)	5.53d	2.53s	5.54d
14-H	5.45d(12)	5.32d	5.41d(12)	5.32d	—	5.44d
15-H	1.24d	1.28d	1.28d	1.32d	1.17s	1.19d
R-	2.73q	2.74q	2.72q	2.74q	4.07s	2.71q
	1.35t					
R^1	6.07qq	—	—	2.10s	2.13s	6.07qq
	1.95dq	—	—	—	—	1.96dq
	1.87dq	—	—	—	—	1.93dq
R^2	—	2.09s	6.07qq	2.09s	—	—
	—	—	1.95dq	—	—	—
	—	—	1.85dq	—	—	—

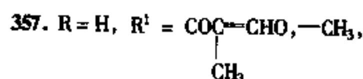


355

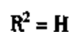


356. $R = H, R^1 = COCH_3$,

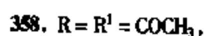
$R^2 = OCOCH_3$



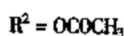
357. $R = H$, R^1 = COC(CH$_3$)=CHO,—CH$_3$,



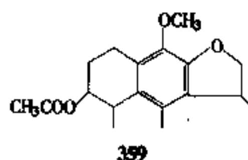
$R^2 = H$



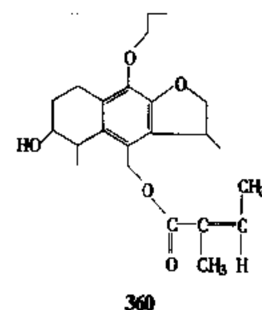
358. $R = R^1 = COCH_3$,



$R^2 = OCOCH_3$



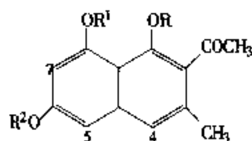
359



360

表 11-32　天然芳环化合物 361～367 的^{1}H-NMR 化学位移[45]

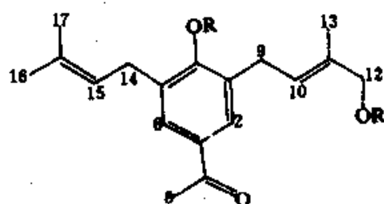
质子 \ 化合物	361	362	363	364	365	366	367
4-H	7.00	6.75	7.35	7.00	6.82	7.28	7.03
5-H	7.00	6.47	6.88	6.90	6.66	6.94	7.01
7-H	6.80	6.39	6.76	6.70	6.50	6.68	6.85
1'-H	5.13	—	5.08	5.02	—	5.00	5.18
OCH_3	—	—	3.86	4.00	4.02	3.90	3.88
			3.76			3.64	
$COCH_3$	2.60	2.63	2.52	2.48	2.55	2.48	2.52
CH_3	2.25	2.46	2.25	2.20	2.30	2.22	2.26



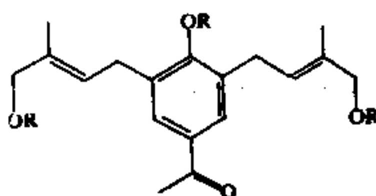
361. R = R² = H, R¹ = β-D-葡萄糖
362. R = R² = CH₃, R¹ = β-D-葡萄糖
363. R = R¹ = R² = H
364. R = H, R² = CH₃, R¹ = β-D-葡萄糖
365. R = R¹ = H, R² = CH₃
366. R = R² = CH₃, R¹ = β-D-葡萄糖
367. R = H, R¹ = CH₃, R² = β-D-葡萄糖

表 11-33 天然芳环化合物 368～373 的¹H-NMR 化学位移[46]

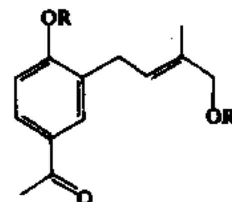
质子 \ 化合物	368	369	370	371	372	373
2-H	7.70s	7.75s	7.64s	7.70s	7.80d(2)	7.90d(2)
6-H	7.70s	7.75s	7.64s	7.70s	7.70dd(8,2)	7.85dd(8,2)
5-H	—	—	—	—	7.16d(8)	7.16d(8)
8-H	2.52s	2.58s	2.46s	2.57s	2.48s	2.57s
9-H	3.48d(8)	3.38d(8)	3.47d(7)	3.36d(7)	3.44d(8)	3.36d(8)
10-H	5.35t(8)	5.53t(8)	5.38t(7)	5.50t(7)	5.62t(8)	5.60t(8)
12-H	4.40bs	4.72bs	4.24s	4.70s	4.00s	4.52s
14-H	3.32d(7)	3.25d(7)	3.47d(7)	3.36d(7)	3.42t(8)	3.36t(8)
15-H	5.30t(8)	5.30t(7)	5.38t(7)	5.50t(7)	—	—
13,16,17-H	1.75～1.78bs	1.75～1.80s	—	—	1.75bs	1.76bs
芳-OCOCH₃	—	2.38s	—	2.35s	—	2.34s
脂-OCOCH₃	—	2.10s	—	2.08s	—	2.08s



368. R = H
369. R = COCH₃



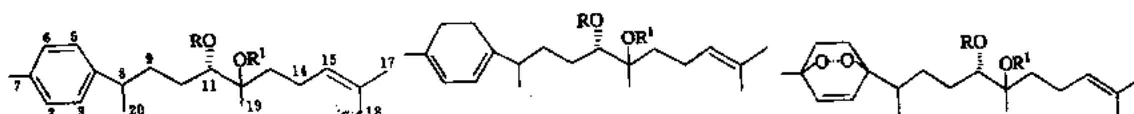
370. R = H
371. R = COCH₃



372. R = H
373. R = COCH₃

表 11-34 天然芳环化合物 374～381 的¹H-NMR 化学位移[47]

质子 \ 化合物	374	375	376	377	378	379	380	381
2-H	7.09s	5.60bs	7.10bd	5.61bd	7.09s	5.61bs	6.42d	6.42d
3-H	7.09s	5.60bs	7.10bd	5.57d	7.09s	5.61bs	6.52d	6.52d
5,6-H	7.09s	2.07bs	7.04bd	2.05m	7.09s	2.07bs	—	—
7-H	2.32s	1.77bs	2.31s	1.77bs	2.32s	1.78bs	1.37s	1.38s
8-H	2.61tq	2.07m	2.61tq	2.05m	2.66tq	2.07m	2.05m	2.05m
11-H	3.35bd	3.39bd	4.84m	4.84m	3.66dd	3.71dd	3.41bd	3.72bt
14-H	2.07m	2.07m	2.05m	2.05m	2.07m	2.07m	2.05bdt	2.05dt
15-H	5.10bt	5.12bt	5.05bt	5.08bt	5.05bt	5.09bt	5.12bt	5.09bt
17-H	1.58bs	1.62bs	1.58bs	1.61bs	1.58bs	1.62bs	1.62bs	1.61bs
18-H	1.68bs	1.69bs	1.67bs	1.68bs	1.68bs	1.69bs	1.69bs	1.69bs
19-H	1.05s	1.10s	1.08s	1.13s	1.00s	1.06s	1.12s	1.07s
20-H	1.05s	1.03s	1.08s	1.13s	1.25d	1.04d	1.00d	1.02d



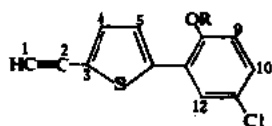
374. R = R¹ = H
375. R = $COCH_3$, R¹ = H
376. R = R¹ = $>C(CH_3)_2$

377. R = R¹ = H
378. R = $COCH_3$, R¹ = H
379. R = R¹ = $>C(CH_3)_2$

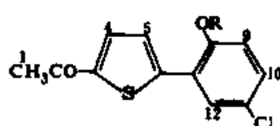
380. 1,4α-O-, R = R¹ = H
381. 1,4α-O-, R = R¹ = $>C(CH_3)_2$

表 11-35 天然芳环化合物 382~387 的¹H-NMR 化学位移[48]

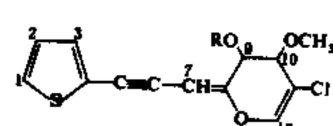
化合物 质子	382	383	384	385	386	387	化合物 质子	382	383	384	385	386	387
1-H	3.42s	3.43s	2.54s	2.58s	7.28dd	7.26dd	9-H	6.87d	7.11d	7.08d	7.33d	4.99dd	6.03dd
2-H	—	—	—	—	6.99dd	6.98dd	10-H	7.18dd	7.30dd	7.24dd	7.49dd	4.24bd	4.20bd
3-H	—	—	—	—	7.20bdd	7.18dd	12-H	7.44d	7.61d	7.78d	7.86d	5.55d	5.57d
4-H	7.29d	7.26d	7.84d	7.89d	—	—	$OCOCH_3$	—	2.35s	—	2.35s	—	2.13s
5-H	7.24d	7.21d	7.76d	7.64d	—	—	OCH_3	—	—	—	—	3.45s	3.45s
7-H	—	—	—	—	5.61bd	5.68bs							



382. R = H
383. R = $COCH_3$



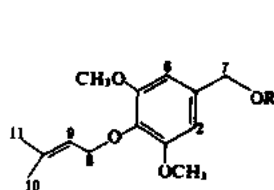
384. R = H
385. R = $COCH_3$

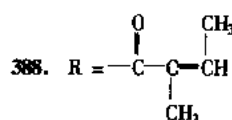


386. R = H
387. R = $COCH_3$

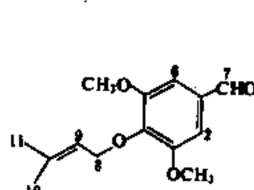
表 11-36 天然芳环化合物 388~392 的¹H-NMR 化学位移[49]

化合物 质子	388	389	390	391	392	化合物 质子	388	389	390	391	392
2,6-H	6.60s	6.59s	6.56s	7.13s	6.74s	10	1.67bs	1.68bs	1.68bs	1.67bs	1.68bs
7-H	5.13s	4.63s	5.03s	9.88s	5.07s	11	1.75bs	1.76bs	1.75bs	1.74bs	1.76bs
8	4.49bd	4.49bd	4.48bd	4.62bd	3.36bd	OCH_3	3.85s	3.86s	3.86s	3.92s	3.82s 3.76s
9	5.57bt	5.58bt	5.57bt	5.56bt	5.05bt						

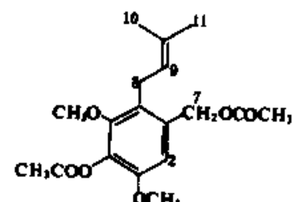


388. R =


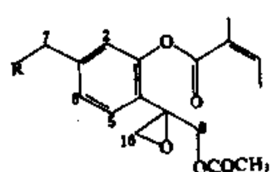
389. R = H
390. R = $COCH_3$



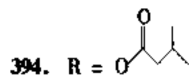
391

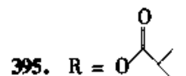


392



393. R = H

394. R = 

395. R = 

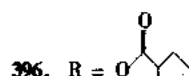
396. R = 

表 11-37 天然芳环化合物 393～396 的 ^{1}H-NMR 化学位移[50]

质子 \ 化合物	393	394	395	396
2-H	6.94bs	7.13bs	7.13bs	7.13bs
5-H	7.38d	7.51d	7.51d	7.51d
6-H	7.07bd	7.25bd	7.24bd	7.24bd
7-H	2.37bs	5.12bs	5.12bs	5.12bs
9-H_A	4.54d	4.54d	4.54d	4.54d
9-H_B	4.20d	4.20d	4.20d	4.20d
10-H_A	3.03d	3.05d	3.06d	3.06d
10-H_B	2.83d	2.84d	2.84d	2.84d
$OCOCH_3$	2.03s	2.01s	2.01s	2.01s
O-当归酰	6.30q	6.33qq	6.33qq	6.33qq
	2.09dq	2.09dq	2.09dq	2.09dq
OCOR	2.07bs	2.07bs	2.07bs	2.07bs
	—	2.61qq	2.43tq	2.26bd
	—	1.20d	1.70ddq	2.08m
	—	—	1.52ddq	0.97d
	—	—	0.91t	—
	—	—	1.18d	—

表 11-38 天然芳香化合物 397～401 的 ^{1}H-NMR 化学位移[93]

质子 \ 化合物	397	398	399	400	401
2-H	—	—	5.34br dd (8.2,9.3)	7.70d (2.0)	7.10s
3-H	7.41s	6.50br s	3.42dd (8.2,15.8); 3.13dd (9.3,15.8)	6.86d (2.0)	—
4-H	7.04s	6.96s	7.44d(2.0)	7.86d (1.2)	—
6-H	—	—	7.43d(2.0)	7.49d (1.2)	—
7-H	7.03s	7.01s	—	—	—
9-H	—	—	—	—	7.64s
10-H	—	4.97br q (6.6)	—	—	—
11-H	2.55s	1.61d (6.6)	1.78br s	2.67s	—
12-H	—	—	5.00br s; 5.11br s		7.37br s
13-H			—		2.50br s
14-H			2.55s		2.76s
15-H			—		2.62s
OMe	3.94s	3.90s	—	4.06s	4.09s
	3.92s	3.90s			4.11s
Ar-OH	—	—	6.45br s		—

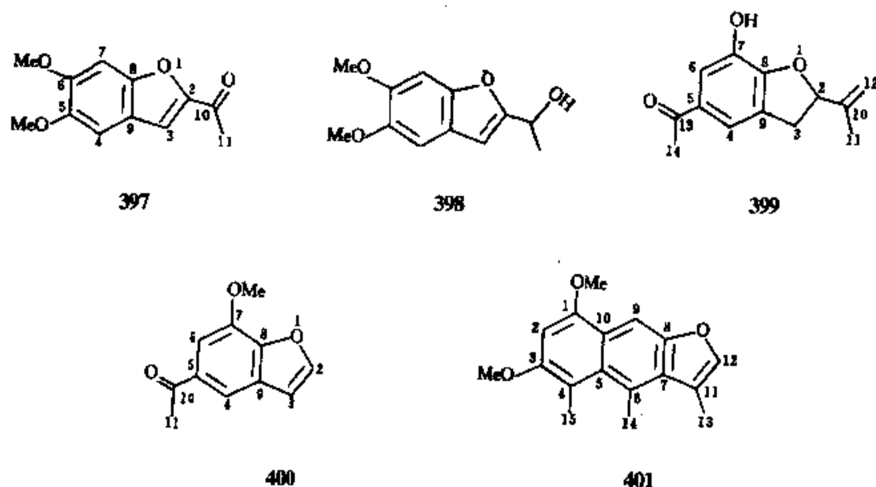
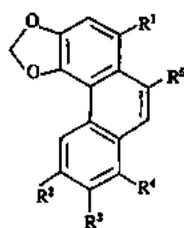
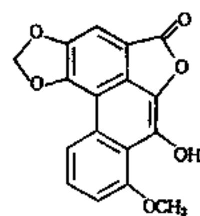


表 11-39 天然菲类衍生物 402～409 的 ^{1}H-NMR 化学位移[94]

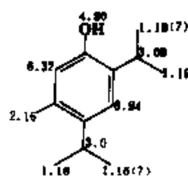
质子 化合物	1,10-H	2-H	3-OCH$_3$	5-H	6-H	7-H	8-H	9-H
402	13.30(COOH)	7.76s	6.46s	9.44d(8)	7.87t(8)	7.77t(8)	8.21d(8)	8.55s
403	COOH	7.77s	6.47s	8.62d(8)	7.77t(8)	7.35d(8)	4.02s(OCH$_3$)	8.55s
404	CONH 10.79s	7.62s	6.46s	8.48d(8)	7.57t(8)	7.94t(8)	7.48t(8)	7.11s
405	CONH 10.74s	7.62s	6.40s	8.09d(8)	7.48t(8)	7.18t(8)	4.00s(OCH$_3$)	7.32s
406	13.32(COOH) 2.48s(CH$_2$)	7.77s	6.45s	8.62d (8.5)	7.82t (8.5)	7.33d (8.5)	4.01s(OCH$_3$)	8.54s
407	COOH	7.66s	6.41s	8.65d (8.5)	7.45d (8.5)	OH 10.28bs	3.92s(OCH$_3$)	8.39s
408	COOH	7.77s	6.50s	8.51s	OH	7.30d (8.5)	8.10d (8.5)	8.51s
409	—COO—	7.77s	6.47s	8.21d(8)	7.64t(8)	7.34d(8)	4.04s(OCH$_3$)	OH 9.97brs



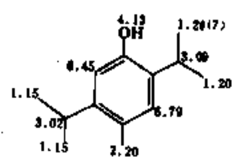
	R^2	R^3	R^4	R^1	R^5
402.	H	H	H	COOH	NO$_2$
403.	H	H	OCH$_3$	COOH	NO$_2$
404.	H	H	H	- CONH -	
405.	H	H	OCH$_3$	- CONH -	
406.	H	H	OCH$_3$	CH$_2$COOH	NO$_2$
407.	H	OH	OCH$_3$	COOH	NO$_2$
408.	OH	H	H	COOH	NO$_2$



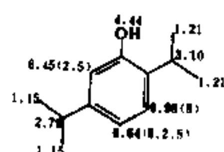
409



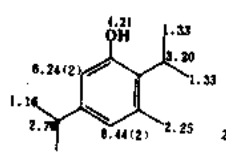
410[51]



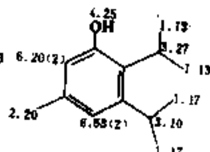
411[51]



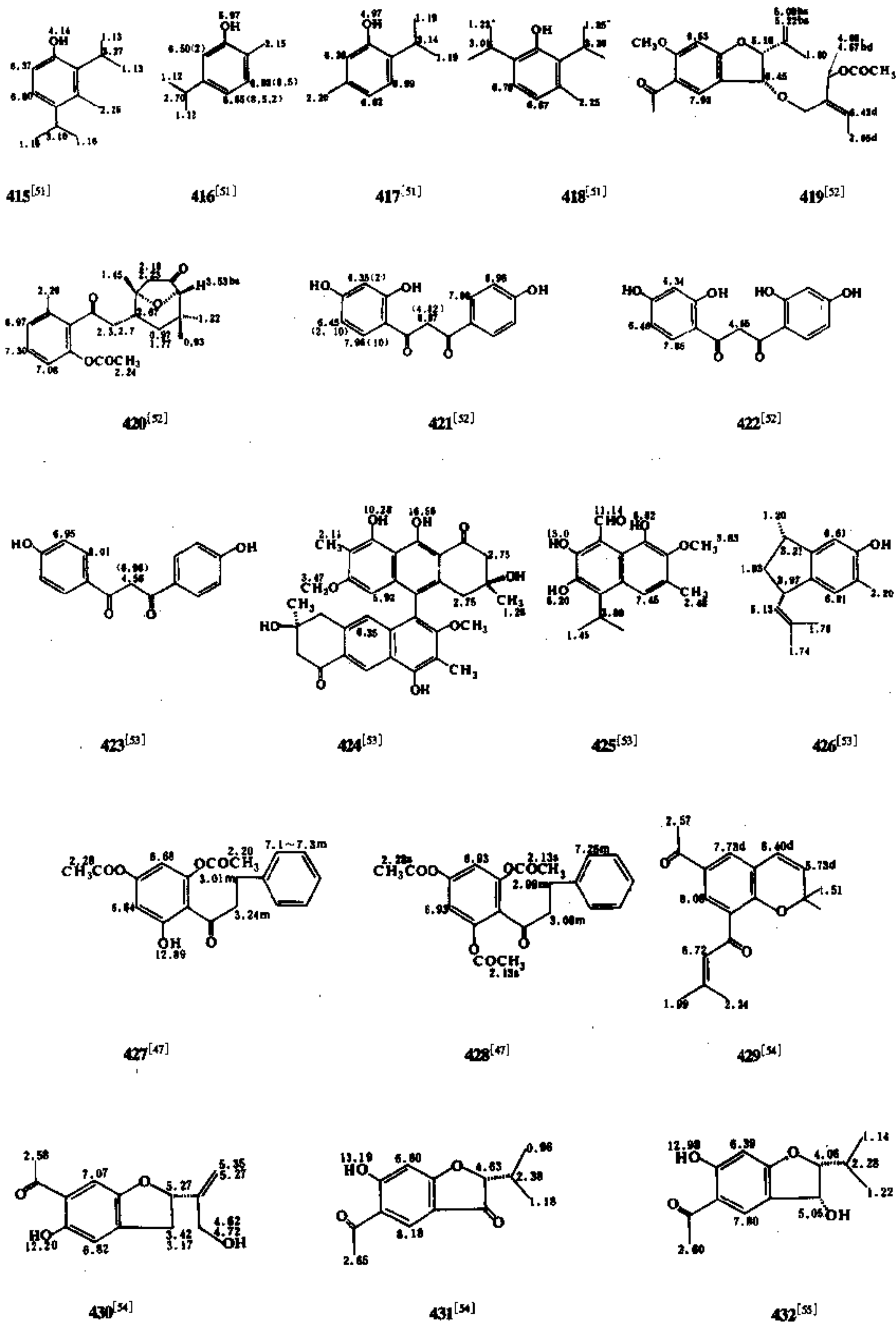
412[51]



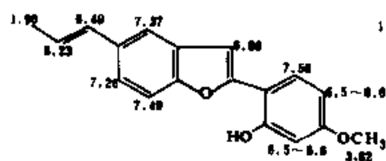
413[51]



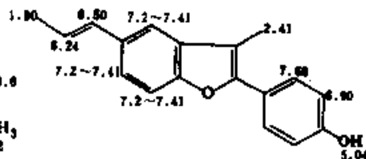
414[51]



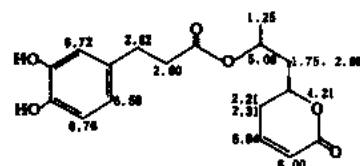
* 表示二个数字可相互调换。



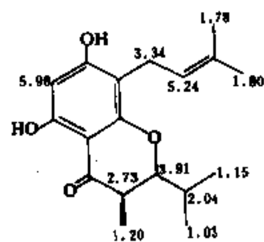
433[55]



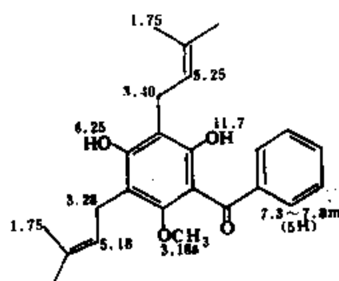
434[55]



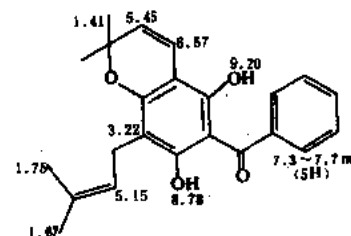
435[41]



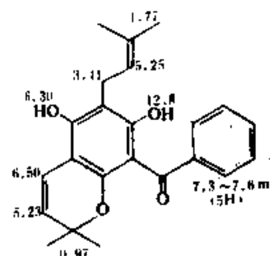
436[60]



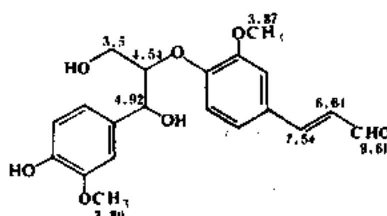
437[41]



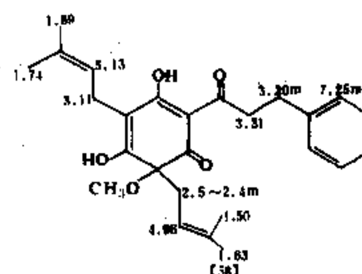
438[41]



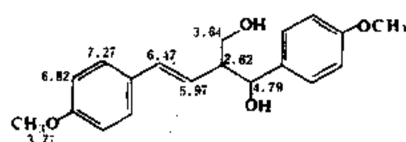
439[56]



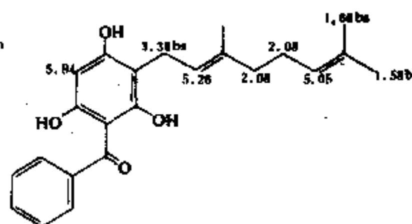
440[57]



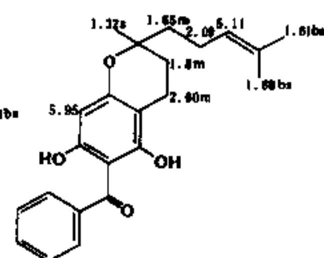
441[58]



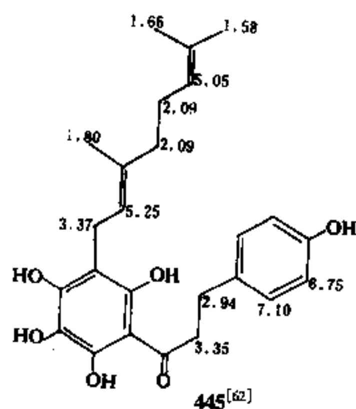
442[59]



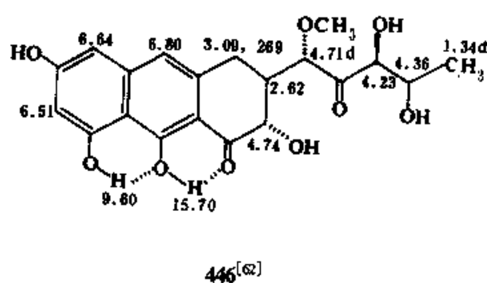
443[61]



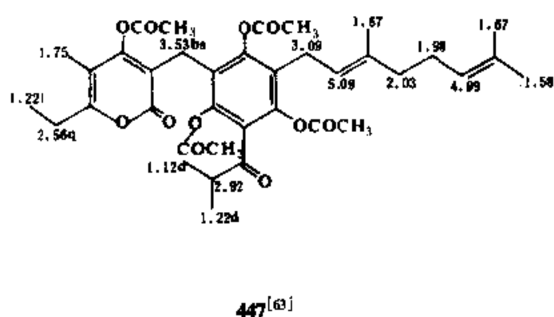
444[61]



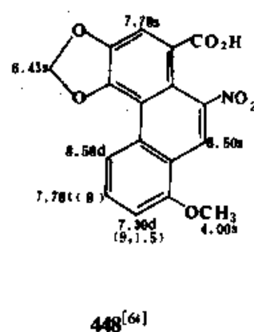
445[62]



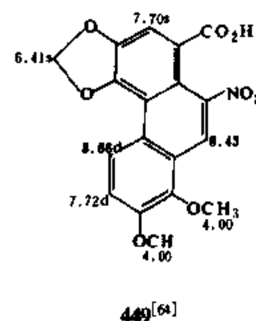
446[62]



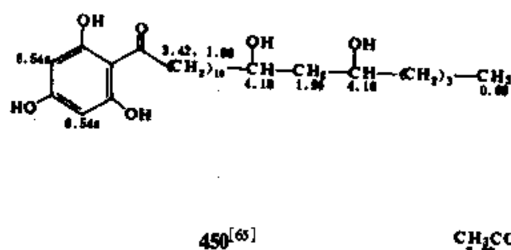
447[63]



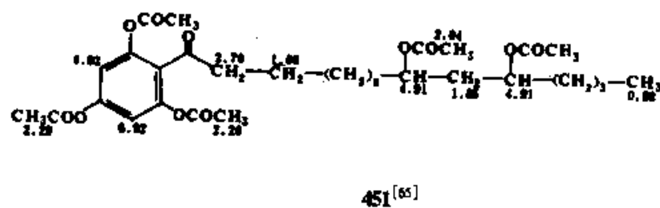
448[64]



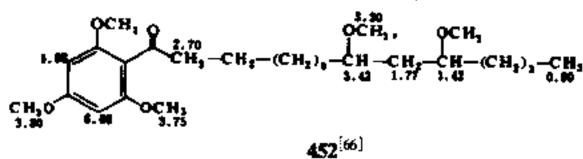
449[64]



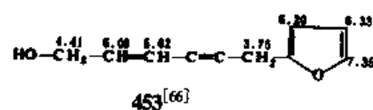
450[65]



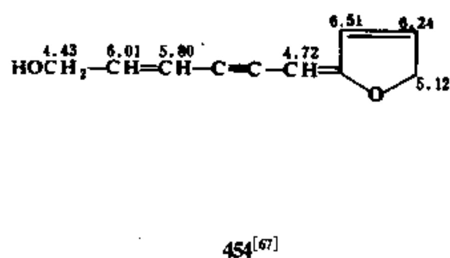
451[65]



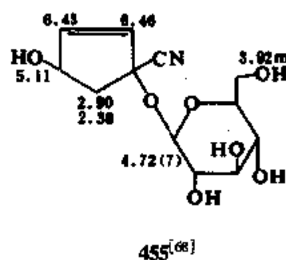
452[66]



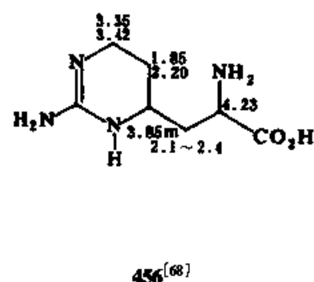
453[66]



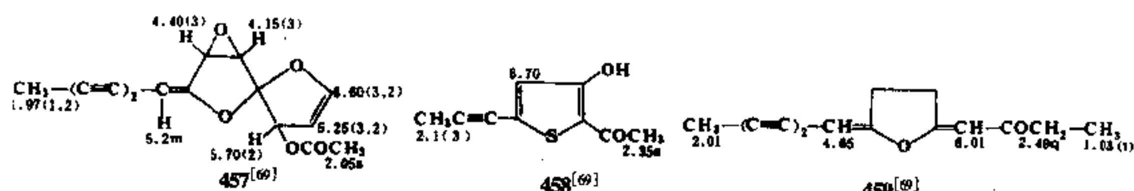
454[67]



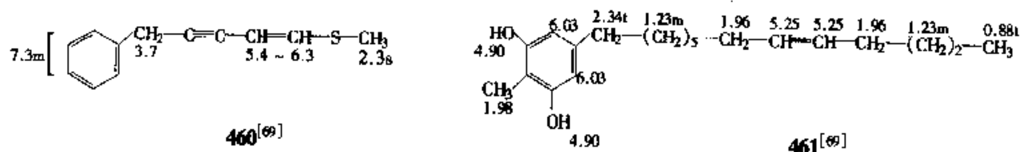
455[68]



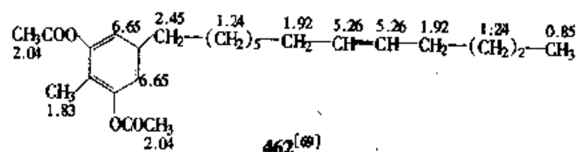
456[68]



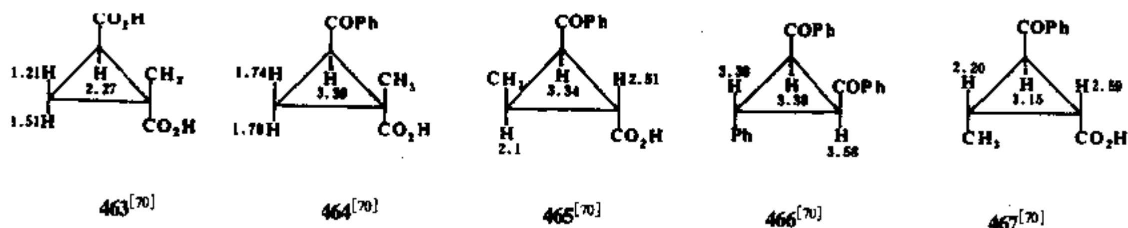
457[69] 458[69] 459[69]



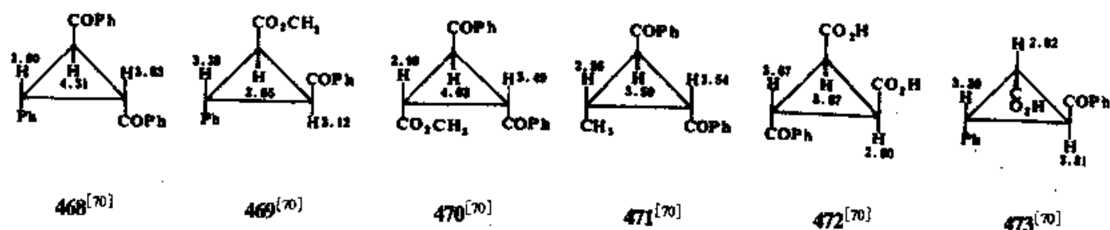
460[69] 461[69]



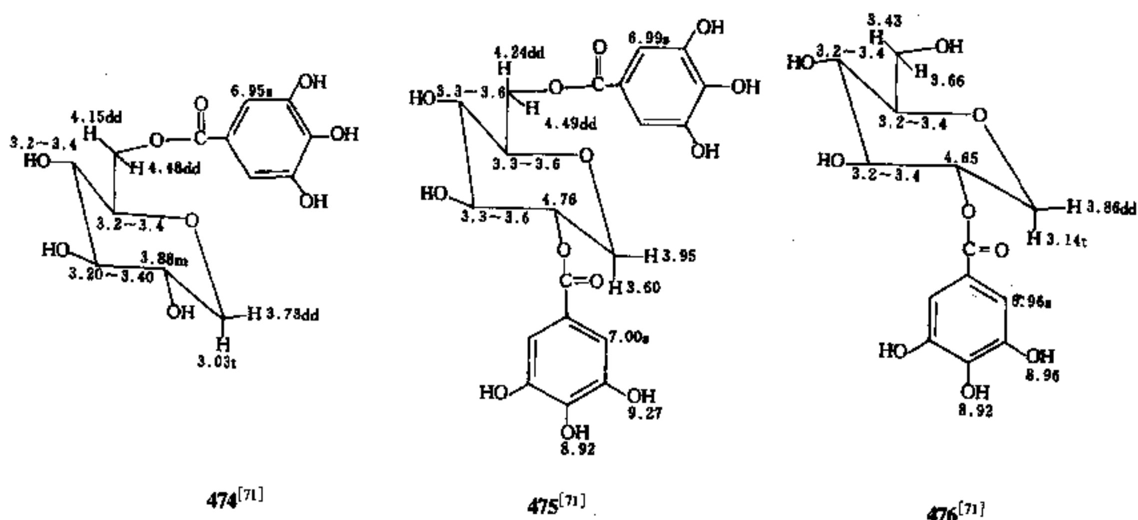
462[69]



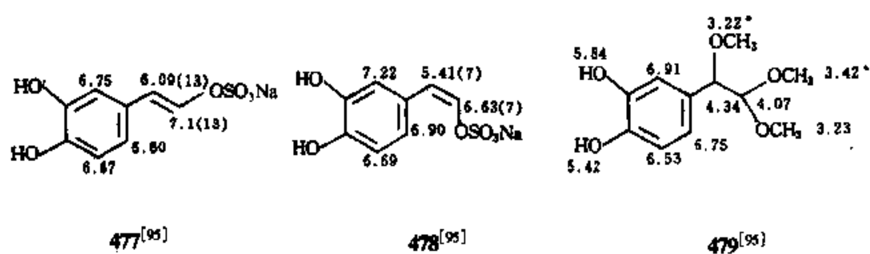
463[70] 464[70] 465[70] 466[70] 467[70]



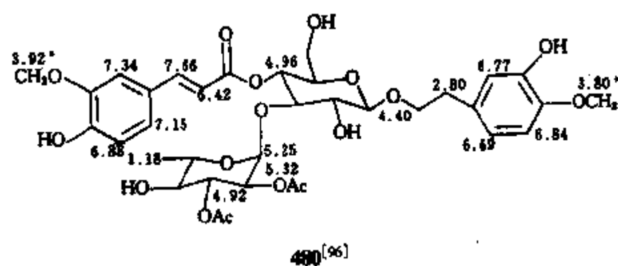
468[70] 469[70] 470[70] 471[70] 472[70] 473[70]



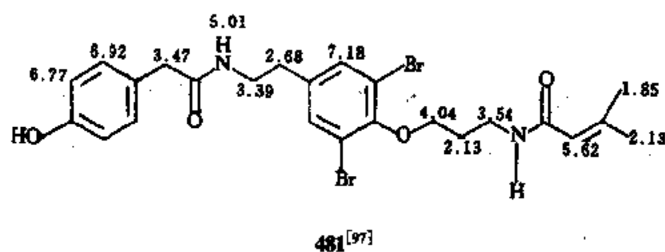
474[71] 475[71] 476[71]



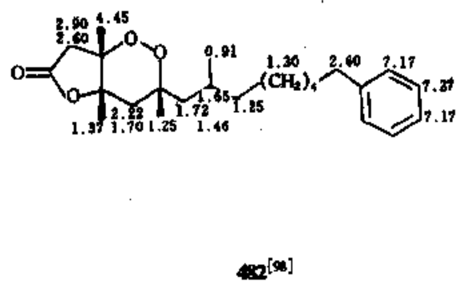
477[95] 478[95] 479[95]



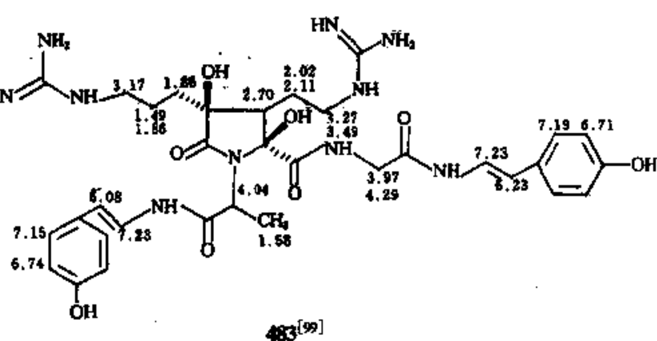
480[96]



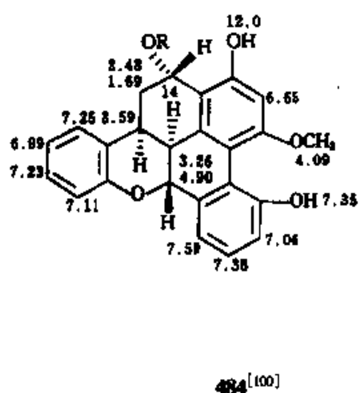
481[97]



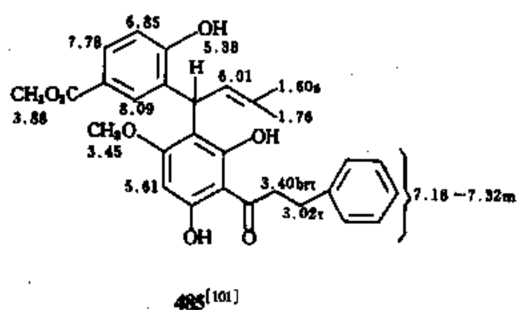
482[98]



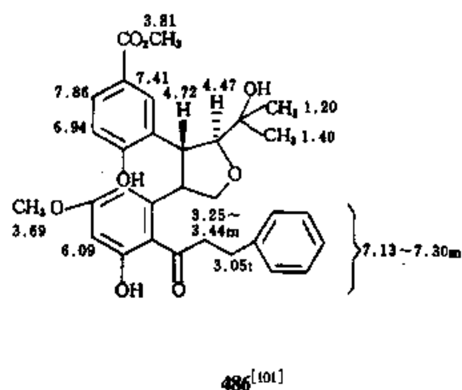
483[99]



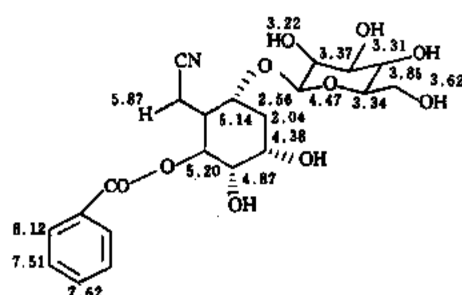
484[100]



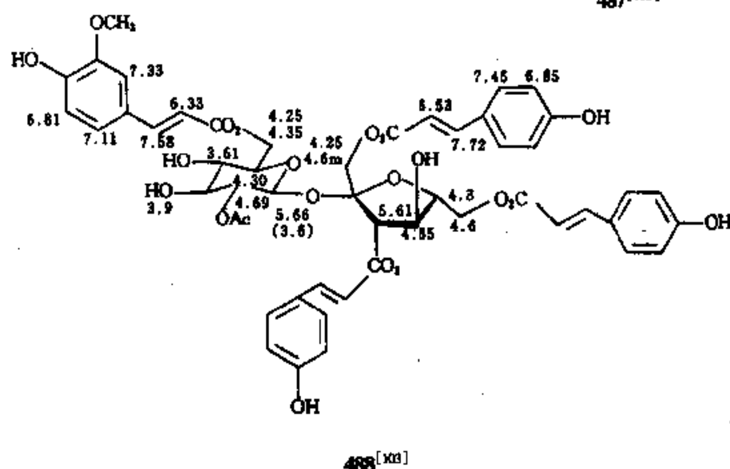
485[101]



486[101]



487[102]

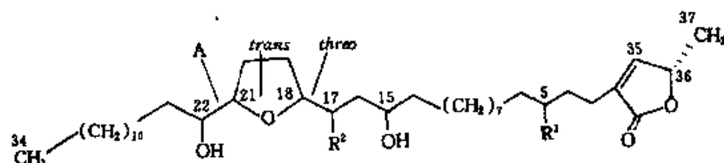


488[103]

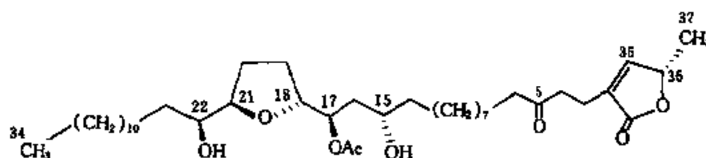
第六节 番荔枝内酯化合物的^{1}H-NMR化学位移

表 11-40 单四氢呋喃环番荔枝内酯化合物489～494的^{1}H-NMR化学位移[104]

质子＼化合物	489	490	491	492	493	494
3-H	2.55m	2.56m	2.53m	2.40m	2.42m	2.40m
4-H	2.71m	2.70m	2.68m	1.62m	1.64m	1.60m
5-H	—	—	—	3.60m	3.59m	3.55m
6-H	2.38t(7.0)	2.38t(7.0)	2.37t(7.0)	1.45m	1.45m	1.45m
7-H	1.54m	1.60m	1.53m	1.25br	1.25br	1.21br
8～13-H	1.25～1.60m	1.25～1.61m	1.23～1.60m	1.25br	1.25br	1.21br
14-H	1.25～1.60m	1.25～1.61m	1.23～1.60m	1.50m	1.50m	1.48m
15-H	3.80m	3.81m	3.36m	3.80m	3.81m	3.36m
16-H	1.54m	1.60m	1.53m	1.58m	1.61m	1.58m
17-H	3.73m	3.76m	5.08m	3.73m	3.75m	5.06m
18,21-H	3.89,3.89m	3.88,3.88m	3.84,3.84m	3.90,3.90m	3.88,3.88m	3.84,3.84m
19,20-H	1.60～2.00m	1.67,1.98m	1.61～1.96m	1.70～2.00m	1.71～2.00m	1.67～1.94m
22-H	3.89m	3.41m	3.84m	3.90m	3.41m	3.84m
23-H	1.25～1.60m	1.25～1.61m	1.23～1.60m	1.35m	1.35m	1.32m
24～33-H	1.25～1.60m	1.25～1.61m	1.23～1.60m	1.25br	1.25br	1.22br
34-H	0.88t(7.0)	0.87t(7.0)	0.85t(6.8)	0.88t(7.0)	0.87t(7.0)	0.85t(6.8)
35-H	7.05d(1.5)	7.04d(1.5)	7.03d(1.4)	7.03d(1.5)	7.04d(1.5)	7.03d(1.4)
36-H	4.98dq(7.0,1.5)	4.98dq(7.0,1.5)	4.96dq(6.8,1.5)	5.00dq(7.0,1.5)	4.98dq(7.0,1.5)	4.96dq(6.8,1.5)
37-H	1.39d(7.0)	1.37d(7.0)	1.37d(6.8)	1.40d(7.0)	1.37d(7.0)	1.37d(6.8)
AcO	—	—	2.05s	—	—	2.05s



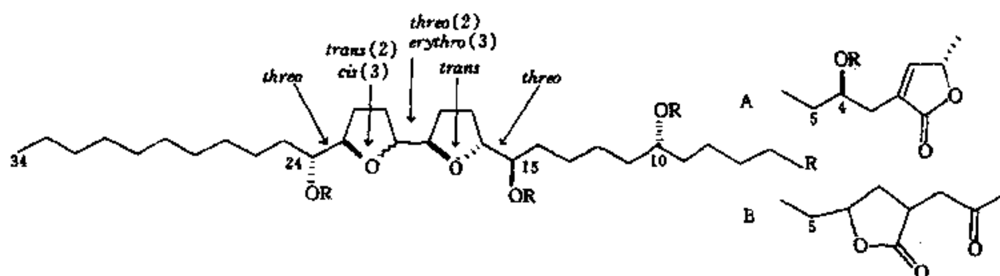
	R^1	R^2	A
489.	=O	OH	*erythro*
490.	=O	OH	*threo*
492.	OH	OH	*erythro*
493.	OH	OH	*threo*
494.	OH	OAc	*erythro*



491

表 11-41 双四氢呋喃环番荔枝内酯化合物 495～498 的^{1}H-NMR 化学位移[105]

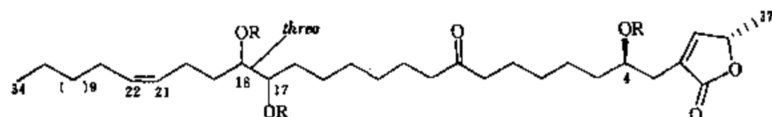
质子＼化合物	495	496	497	498
1-H				
2-H		3.04m,3.02m		3.04m,3.02m
3a-H	2.53dddd(15.1,3.5,1.4,1.4)	2.60m,2.24m	2.53dddd(15.5,3.5,1.5,1.5)	2.60m,2.23m
3b-H	2.41dddd(15.1,8.3,1.4,1.4)	1.50m,1.98m	2.40dddd(15.5,8.0,1.5,1.5)	1.50m,1.98m
4-H	3.86m	4.39m,4.55m	3.83m	4.39m,4.56m
5-H	1.49m	1.75m,1.48m, 1.69m,1.57m	1.49m	1.75m,1.48m 1.69m,1.57m
6～8-H	1.20～1.60m	1.20～1.60m	1.20～1.60m	1.20～1.60m
9-H	1.41m	1.41m	1.41m	1.41m
10-H	3.60m	3.59m	3.59m	3.60m
11-H	1.41m	1.41m	1.43m	1.42m
12～13-H	1.20～1.60m	1.22～1.50m	1.20～1.60m	1.22～1.50m
14-H	1.41m	1.41m	1.41m	1.41m
15-H	3.39m	3.39m	3.39m	3.39m
16-H	3.86m	3.85m	3.83m	3.83m
17-H	1.64m,1.98m	1.64m,1.98m	1.77m,1.96m	1.77m,1.96m
18-H	1.64m,1.98m	1.64m,1.98m	1.86m,1.94m	1.86m,1.94m
19-H	3.86m	3.85m	3.97ddd(7.0,6.5,5.0)	3.97ddd(7.0,6.5,5.0)
20-H	3.86m	3.85m	4.05ddd(8.5,6.0,5.0)	4.05ddd(8.5,6.0,5.0)
21-H	1.64m,1.98m	1.64m,1.98m	1.69m,2.04m	1.69m,2.04m
22-H	1.64m,1.98m	1.64m,1.98m	1.74m,1.96m	1.74m,1.96m
23-H	3.86m	3.85m	3.83m	3.83m
24-H	3.39m	3.39m	3.39ddd(6.5,7.0,6.0)	3.39m
25-H	1.41m	1.41m	1.41m	1.41m
26-H	1.22～1.60m	1.22～1.60m	1.22～1.60m	1.22～1.60m
27～31-H	1.22～1.60m	1.22～1.60m	1.22～1.60m	1.22～1.60m
32-H	1.22～1.60m	1.22～1.60m	1.22～1.60m	1.22～1.60m
33-H	1.22～1.60m	1.22～1.60m	1.22～1.60m	1.22～1.60m
34-H	0.88t(7.0)	0.88t(7.0)	0.88t(7.0)	0.88t(7.0)
35a-H	7.19ddd(1.5,1.5,1.5)	3.11dd(18.5,3.5)	7.19ddd(1.5,1.5,1.5)	3.11dd(18.5,3.5)
35b-H		2.61dd(18.5,8.5)		2.61dd(18.5,8.5)
36-H	5.06qddd(7.0,1.5,1.5,1.5)		5.06qddd(7.0,1.5,1.5,1.5)	
37-H	1.44d(7.0)	2.20s	1.44d(7.0)	2.20s



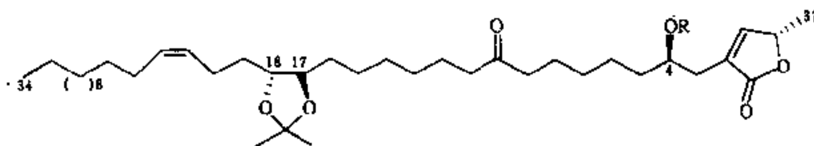
495. A: R = H 2a R = TMSi 2b R = *S*-MTPA 2c R = *R*-MTPA
496. B: R = H 2e R = *S*-MTPA 2f R = *R*-MTPA
497. A: R = H 3a R = TMSi 3b R = *S*-MTPA 3c R = *R*-MTPA
498. B: R = H 3e R = *S*-MTPA 3f R = *R*-MTPA

表 11-42　无四氢呋喃环番荔枝内酯化合物 499 ~ 501 的 ^{1}H-NMR 化学位移[106]

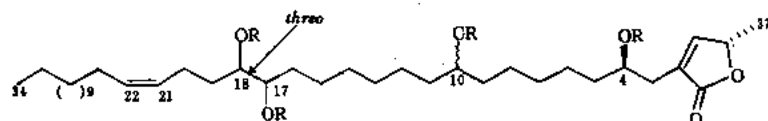
质子 \ 化合物	499	500	501
1-H	—	—	—
2-H	—	—	—
3a-H	2.53ddd(15.0,4.0,1.6,1.6)	2.53ddd(15.0,4.0,1.6,1.6)	2.53ddd(15.0,4.0,1.6,1.6)
3b-H	2.40ddd(15.0,8.0,1.6,1.6)	2.40ddd(15.0,8.0,1.6,1.6)	2.40ddd(15.0,8.0,1.6,1.6)
4-H	3.84m	3.86m	3.86m
5-H	1.50m	1.50m	1.50m
6 ~ 7-H	1.40 ~ 1.20m	1.40 ~ 1.20m	1.40 ~ 1.20m
8-H	1.66m	1.66m	1.40 ~ 1.20m
9-H	2.40m	2.40m	1.74 ~ 1.50m
10-H	—	—	3.59m
11-H	2.40m	2.40m	1.74 ~ 1.50m
12 ~ 15-H	1.60 ~ 1.50m	1.60 ~ 1.50m	1.40 ~ 1.20m
16-H	1.55m	1.55m	1.55m
17-H	3.42m	3.59m	3.44m
18-H	3.42m	3.59m	3.44m
19-H	1.66m	2.03m	1.66m
20-H	2.16m	2.17m	2.16m
21-H	5.36dd(11.0,7.0,6.6)	5.35dd(11.0,7.0,6.6)	5.39dd(11.0,7.0,6.6)
22-H	5.40dd(11.0,7.0,6.5)	5.40dd(11.0,7.0,6.5)	5.40dd(11.0,7.0,6.5)
23-H	2.04m	2.04m	2.04m
24-H	1.25m	1.25m	1.25m
25 ~ 31-H	1.40 ~ 1.20m	1.40 ~ 1.20m	1.40 ~ 1.20m
32-H	1.40 ~ 1.20m	1.40 ~ 1.20m	1.40 ~ 1.20m
33-H	1.23m	1.23m	1.25m
34-H	0.88t(7.0)	0.88t(7.0)	0.88t(7.0)
35-H	7.20q(1.5)	7.19q(1.5)	7.20q(1.5)
36-H	5.06qq(7.0,1.5)	5.07qq(7.0,1.5)	5.06qq(7.0,1.5)
37-H	1.44d(7.0)	1.44d(7.0)	1.44d(7.0)
丙酮甲基	—	1.387s, 1.375s	—



499. R = H



500. R = H



501. R = H

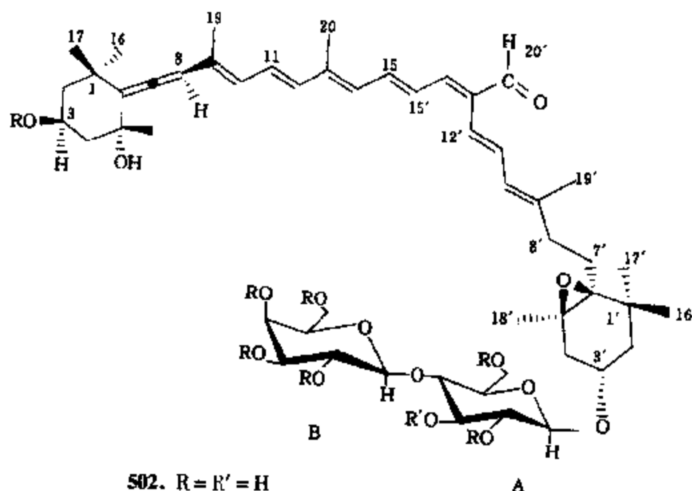
第七节　类胡萝卜素衍生物的¹H-NMR 化学位移

表 11-43　类胡萝卜素化合物 502～504 的¹H-NMR 化学位移[107]

质子＼化合物	502	503	504
2ax-H	1.29, t, $J_{2,2}\approx12$, $J_{2,3}\approx11$	1.42, dd, $J_{2,2}\approx13.2$, $J_{2,3}\approx9.9$	1.42, dd, $J_{2,2}\approx13.0$, $J_{2,3}\approx11.1$
2eq-H	≈1.90, ddd, $J_{2,2}\approx12.5$, $J_{2,3}\approx3.5$, $J_{2,4}\approx1$	≈2.00m	2.01, m
3ax-H	4.20, m	≈5.39, m	≈5.39, m
4ax-H	1.35, dd, $J_{4,4}\approx13$, $J_{4,3}\approx11.5$	1.52, t, $J_{4,4}=J_{4,3}\approx12.0$	1.52, dd, $J_{4,4}=13.0$, $J_{4,3}=11.0$
4eq-H	2.18, ddd, $J_{4,4}=12.5$, $J_{4,3}=5.5$, $J_{4,2}\approx1$	2.29, m	2.29, m
8-H	6.072, s	6.066, s	6.067, s
10-H	6.17, d, $J_{10,11}=11.5$	6.15, d, $J_{10,11}=11.5$	6.15, d, $J_{10,11}=11.7$
11-H	6.81, ddd, $J_{11,12}=15$, $J_{11,10}=11.5$	6.70, dd, $J_{11,12}=14.9$, $J_{11,10}=11.4$	6.71, dd, $J_{11,12}=15.0$, $J_{11,10}=11.4$
12-H	6.42, d, $J_{12,11}=15$	6.37, d, $J_{12,11}=15.0$	6.37, d, $J_{12,11}=15.1$
14-H	6.41, d, $J_{14,15}=11.8$	6.32, d, $J_{14,15}=11.9$	6.32, d, $J_{14,15}=11.8$
15-H	7.24, m	7.06, dd, $J_{15,15'}=13.8$, $J_{15,14}=11.8$	7.06, dd, $J_{15,15'}\approx14$, $J_{15,14}\approx11$
16-H	1.336, 3H, s	1.390, 3H, s	1.390, 3H, s
17-H	1.064, 3H, s	1.077, 3H, s	1.077, 3H, s
18-H	1.309, 3H, s	1.358, 3H, s	1.358, 3H, s
19-H	1.852, 3H, s	1.832, 3H, s	1.832, 3H, s
20-H	2.062, 3H, s	2.043, 3H, s	2.044, 3H, s
2′ax-H	1.34, dd, $J_{2',2'}=13.3$, $J_{2',3'}=10.5$	1.29, dd, $J_{2',2'}=12.5$, $J_{2',3'}=10.1$	1.30, dd, $J_{2',2'}=13.1$, $J_{2',3'}=9.3$
2′eq-H	1.66, ddd, $J_{2',2'}\approx13$, $J_{2',3'}\approx3.5$, $J_{2',4'}\approx1.2$	1.62, ddd, $J_{2',2'}=11.9$, $J_{2',3'}=4.0$, $J_{2,4'}(W)=1.5$	1.64, m

续表

质子＼化合物	502	503	504
3'-H	3.83,m	≈3.74,m	3.72,m
4'ax-H	1.78,dd,$J_{4',4'}$=14.2,$J_{4',3'}$=8.3	1.63,dd,$J_{4',4'}$=14.2,$J_{4',3'}$=8.1	1.65,dd,$J_{4',4'}$=15.1,$J_{4',3'}$=8.2
4'eq-H	2.36,ddd,$J_{4',4'}$=14,$J_{4',3'}$=4.0,$J_{4',2'}$=1.4	2.24,dd,$J_{4,4'}$=14.6,$J_{4',3'}$=5.0	2.24,dd,$J_{4',4'}$=15.0,$J_{4',3'}$=3.1
7'-H_A	1.69,ddd,$J_{7',7'}$=17,$J_{7',8'}$=10and 7.5	≈1.67,m	≈1.67,m
7'-H_B	1.95,ddd,$J_{7',7'}$=17,$J_{7',8'}$=11and 6.5	≈1.89,m	≈1.90,m
8'-H	≈2.30,2H,m	≈2.25,2H,m	≈2.23,2H,m
10'-H	5.98,d,$J_{10',11'}$=11.3	5.94,d,$J_{10',11}$=11.3	5.95,d,$J_{10',11'}$=10.9
11'-H	7.58,dd,$J_{11',12}$=15.3,$J_{11',10'}$=11.1	7.55,dd,$J_{11',12}$=15.4,$J_{11',10'}$=11.1	7.55,dd,$J_{11',12'}$=15.5,$J_{11',10'}$=11
12'-H	6.46,dd,$J_{12',11'}$≈15,$J_{12',20'}$=1.8	6.39,dd,$J_{12',11'}$=15.3,$J_{12',20'}$=2Hz	6.39,dd,$J_{12',11}$=15.2,$J_{12',20}$≈2
14'-H	≈6.97,m	6.80,d,$J_{14',15'}$=11.9	6.80,d,$J_{14',15'}$=11.7
15'-H	≈6.97,m	6.86,dd,$J_{15,15'}$≈13.6,$J_{15',14'}$≈11.8	6.87,dd,$J_{15,15'}$=13.7,$J_{15',14'}$=11.6
16'-H	1.064,3H,s	1.054,3H,s	1.052,3H,s
17'-H	1.226,3H,s	1.156,3H,s	1.159,3H,s
18'-H	1.384,3H,s	1.349,3H,s	1.353,3H,s
19'-H	1.848,3H,s	1.855,3H,s	1.854,3H,s
20'-H	9.49,d,$J_{20',12'}$=2.1	9.535,d,$J_{13',20}$=2.0	9.535,d,$J_{13',12'}$=2.0
	10.300,s,0.06H,all-trans	10.307,s,≈0.1H,顺	10.306,s,≈0.1H,顺
1a-H_A	4.37,d,$J_{1,2}$≈7.3	4.50,d,$J_{1,2}$=8.1	4.43,d,$J_{1,2}$=8.1
2a-H_A	3.19,dd,$J_{1,2}$=8.1,$J_{2,3}$=8.5	4.84,dd,$J_{2,3}$=9.6,$J_{2,1}$=8.1	4.83,dd,$J_{2,3}$=9.6,$J_{2,1}$=8.1
3a-H_A	3.51,dd,$J_{3,4}$~$J_{3,2}$=10	5.18,t,$J_{3,2}$=9.3	3.72,dd,$J_{3,2}$=$J_{3,4}$=9.6,$J_{3\text{-}OH}$=1.7
4a-H_A	3.57,t,$J_{3,4}$=$J_{2,3}$=9	3.74,dd,$J_{4,5}$=9.5,$J_{4,3}$=9.0	3.49,dd,$J_{4,5}$=9.5,$J_{4,5}$=8.0
5a-H_A	3.40,ddd,$J_{4,5}$=9.5,$J_{5,6a}$~$J_{5,6b}$=3	3.59,m	≈3.56,m
6a,b-H_A	3.86,m,2H	≈4.09,m	≈4.00,m
6a,b-H_A		4.46,dd,$J_{6,6}$=11.2,$J_{5,6}$=1.8	4.30,dd,$J_{6,6}$=11.2,$J_{6,5}$=1.6
1b-H_B	4.37,d,J≈7.3	4.48,d,$J_{1,2}$=8.0	4.54,d,$J_{1,2}$=8.0
2b-H_B	3.54,dd,$J_{2,3}$=8.8,$J_{2,1}$=7.5	5.12,dd,$J_{2,3}$=10.5,$J_{2,1}$=7.9	5.25,dd,$J_{2,3}$=10.5,$J_{2,1}$=8.0
3b-H_B	3.48,dd,$J_{3,2}$=9.1,$J_{3,4}$=3.1	4.96,dd,$J_{3,2}$=10.4,$J_{3,4}$=3.5	5.00,dd,$J_{2,3}$=10.5,$J_{3,4}$=3.2
4b-H_B	3.81,d,$J_{4,3}$=3.3	5.35,d,$J_{4,3}$=3.3	5.39,dd,$J_{3,4}$=3.5,$J_{4,5}$<1
5b-H_B	≈3.58,m	3.87,dd,$J_{5,6}$=7.1,$J_{5,6}$=6.5	4.03,m
6a,b-H	3.69,dd,$J_{6,6}$=11.5,$J_{6,5}$=4.5	≈4.08,m	4.11,dd,$J_{6,6}$=11.5,$J_{6,5}$=7.5
6b,b-H	3.78,dd,$J_{6,6}$=11.5,$J_{6,5}$=5.5	≈4.13,m	4.15,dd,$J_{6,6}$=12.0,$J_{6,5}$=5.1
OH			4.25,d,$J_{OH\text{-}3}$=1.7
Ac		1.968,3H,s;2.043,6H,s;2.052,3H,s;2.063,3H,s,2.111,3H,s;2.154,3H,s	1.985,3H,s;2.044,3H,s;2.060,3H,s;2.091,3H,s;2.097,3H,s;2.100,3H,s;2.163,3H,s



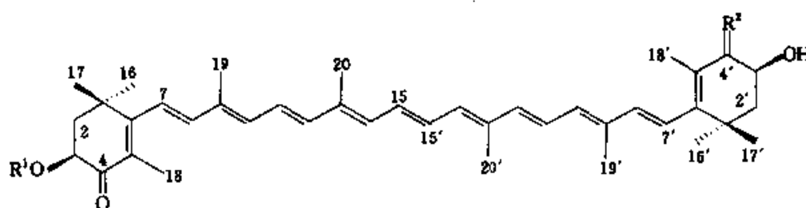
502. R = R' = H

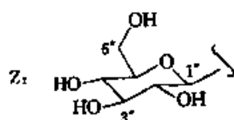
503. R = R' = Ac

504. R = Ac, R' = H

表 11-44 类胡萝卜素化合物 505,506 的^{1}H-NMR 化学位移[108]

质子＼化合物	505	506
2-H_2	2.04t(14)	2.04m
	2.15dd(6,14)	2.15dd(6,14)
3-H	4.40dd(6,14)	4.40dd(6,14)
16-H_3	1.35s	1.35s
17-H_3	1.23s	1.23s
18-H_3	1.91s	1.91s
2'-H_2	1.81t(13)	1.48t(12)
	2.16dd(6,13)	1.77ddd(2,4,12)
3'-H	4.32ddd(2,6,13)	4.00m
4'-H_2	—	2.05m
	—	2.39ddd(2,6,17)
16'-H_3	1.32s	1.08s
17'-H_3	12.1s	1.08s
18'-H_3	1.94s	1.74s
7-H	6.21d(16)	6.20d(16)
7'-H	6.22d(16)	6.12s
8-H	6.44d(16)	6.44d(16)
8'-H	6.44d(16)	6.12s
10-H	6.30m	6.30m
10'-H	6.30m	6.16d(11)
11-H	6.65m	6.65m
11'-H	6.65m	6.67m
12-H	6.45d(15)	6.45d(15)
12'-H	6.45d(15)	6.36d(15)
14-H	6.30m	6.30m
14'-H	6.30m	6.26d(11)
15-H	6.67m	6.67m
15'-H	6.67m	6.66m
19,20,19',20'-H_3	1.99~2.01s	1.98~2.00s
1''-H	4.57d(8)	4.57d(8)
2''-H	3.45dd(8,9)	3.45dd(8,9)
3''-H	3.61m	3.61m
4''-H	3.61m	3.61m
5''-H	3.41m	3.41m
6''-H_2	3.83m	3.83m
	3.93m	3.93m



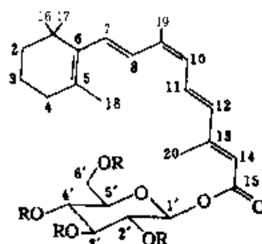


505. R^1 = Z, R^2 = O

506. R^1 = Z, R^2 = H_2

表 11-45　维甲酸类化合物 507,508 的^{1}H-NMR 化学位移[109]

质子＼化合物	507	508	质子＼化合物	507	508
2-H	1.48m	1.48m	19-H	2.02br s	2.03br s
3-H	1.63m	1.63m	20-H	2.34br s	2.34br s
4-H	2.05m	2.08m	1′-H	5.54d,8.5	5.94d(8.5)
7-H	6.80d(16)	6.80d(16)	2′-H	3.35dd,8.5	5.08m
8-H	6.35d(16)	6.36d(16)	3′-H	3.48dd,8.5	5.39dd(9)
10-H	6.15d(12)	6.15d(12)	4′-H	3.40dd,8.5	5.08m
11-H	7.29dd(12,15)	7.32dd(12,15)	5′-H	3.39m	4.13m
12-H	6.39d(15)	6.39d(15)	6′-H	3.66dd,12,1	4.09dd(12,5)
14-H	5.82s	5.78s		3.79dd,12,3.5	4.26dd(12,1.5)
16-H	1.03s	1.03s	CH_3(Ac)		1.95s
17-H	1.03s	1.03s			1.97s
18-H	1.74br s	1.74br s			2.00s



507. R = H

508. R = Ac

第八节　前列腺素和大环内酯类化合物的^{1}H-NMR 化学位移

一、前列腺素类化合物的^{1}H-NMR 化学位移

表 11-46　前列腺素类化合物 509～515 的^{1}H-NMR 化学位移[110]

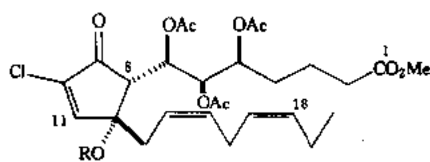
质子＼化合物	509	510	511	512	513	514	515
2-H_2	2.2m	2.3s	2.3m	2.3t	2.3m	2.3t	2.3m
3-H_2	1.6m	1.6m	1.6m	1.6m	1.6m	1.6m	1.6m
4-H_2	1.6m	1.6m	1.6m	1.6m	1.6m	1.6m	1.6m
5-H	5.18ddd (5.3,5.3,7.5)	5.3m	5.18ddd (5.3,5.3,7.5)	5.27br dt (1.1)	5.25m	5.2m	5.25m
6-H	5.61dd (5.3,5.3)	5.3m	5.61dd (5.3,5.3)	5.33dd (1.1,7.8)	6.02dd (4.3,9.1)	5.86dd (4.1,9.4)	6.01dd (4.3,9.1)
7-H	5.34dd (4.2,5.3)	5.3m	5.31dd (4.2,5.3)	5.50dt (1.7,7.8)	6.35d (9.1)	6.47d (9.4)	6.33d (9.1)
8-H	2.75d (4.2)	3.1d	2.74d (4.2)	3.01d (1.7)			
11-H	7.26s	7.8s	7.26s	7.82s	7.27s	7.59s	7.25s
13-H_a	2.53dd (7.0,14.7)	3.5dd	2.48dd (7.3,14.4)	2.87dd (8.3,10.2)	3.01dd (8.1,14.3)	3.33dd (8.7,14.0)	2.95dd (8.5,13.5)
13-H_b	2.45dd (8.1,14.7)	2.9dd	2.40dd (7.9,14.4)	2.77dd (8.3,10.2)	2.68dd (7.0,14.3)	2.8dd (6.6,14.0)	2.62dd (7.2,13.5)
14-H	5.30ddd (7,8.1,10.8)	5.3m	5.25ddd (7.3,7.9,10.9)	5.10dt (2.4,7.8)	5.25m	5.2m	5.25m

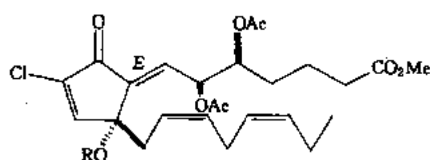
续表

质子 \ 化合物	509	510	511	512	513	514	515
15-H	5.61dt (7,10.8)	5.7dt	5.63dt (7,10.9)	5.58dt (2.4,7.8)	5.53m	5.46dt (7.0,10.6)	5.52dt (6.7,10.9)
16-H_2	2.78m	2.8t	1.95m	2.09m	2.74br dd (7.1,7.1)	2.70t (7.0)	2.0m
17-H	5.24dt (1,7,10.6)	5.3m	1.26m	1.26m	5.2m	5.2m	1.3m
18-H	5.41dt (7,10.6)	5.6dt	1.26m	1.26m	5.41m	5.38ddd (2,7,10.2)	1.3m
19-H_2	2.05m	2.1m	1.26m	1.26m	2.05m	1.9m	1.3m
20-H_3	1.00t (7.5)	0.9t	0.85t (6.7)	0.86t (6.0)	0.94t (7.5)	0.94t (7.5)	0.86t (7.1)
OMe	3.65s	3.6s	3.65s	3.65s	3.65s	3.63s	3.63s
OAc	2.11s	2.2s	2.09s	2.14s	2.09s	2.10s	2.10s
OAc	2.08s	2.1s	2.06s	2.05s	2.05s	2.08s	2.05s
OAc	2.00s	2.0s	1.98s	1.99s		2.05s	
OAc		1.9s		1.90s			
OH^c	3.57s		3.48s		3.50s		3.63s

表 11-47 前列腺素类化合物 516 ~ 521 的 ^{1}H-NMR 化学位移[110]

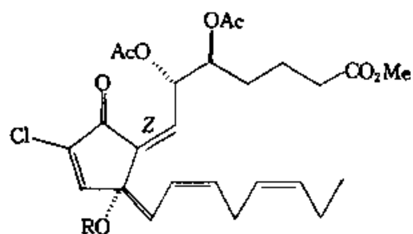
质子 \ 化合物	516	517	518	519	520	521
2-H_2	2.3m	2.3m	2.3m	2.3m	2.3m	2.3m
3-H_2	1.6m	1.6m	1.6m	1.6m	1.6m	1.6m
4-H_2	1.6m	1.6m	1.6m	1.6m	1.6m	1.6m
5-H	5.07m	5.1m	5.18dt(3.4)	5.2m(3.4)	5.2m	5.2m
6-H	5.86dd(4.1,9.2)	6.32dd(3.5,7.7)	6.46dd(3.4,7.7)	6.32dd(3.6,7.8)	6.46dd(3.9,7.8)	5.98dd(4.2,9.0)
7-H	6.47d(9.2)	6.08d	6.1d	6.07d	6.09d	6.54d(9.0)
11-H	7.6s	7.20s	7.53s	7.20s	7.53s	3.96s
13-H_A	3.31dd (6.6,14.3)	2.59dd (7.7,14.5)	2.88dd (6.7,14.5)	2.56dd (8,14)	2.86dd	2.8m
13-H_b	2.77dd (6.6,14.3)	2.47dd (7.3,14.5)	2.63dd (6.7,14.5)	2.44dd (8,14)	2.58dd	2.8m
14-H	5.1dt(6.6,10.7)	5.1m	5.15ddd (6.7,7.5,10.6)	5.2m	5.2m	5.2m
15-H	5.49dt (6.7,10.7)	5.36dt (7.2,10.9)	5.53dt (7.3,10.6)	5.57dt (7.6,10.9)	5.54dt (8.8,10.7)	5.58m
16-H_2	1.94t(6.7)	2.74dd(6.4,7.2)	2.73t(4.8)	1.97m	1.9m	2.7m
17-H	1.3m	5.1m	5.20dt (4.8,10.5)	1.3m	1.3m	5.2m
18-H	1.3m	5.2m	5.40dt (7.0,10.5)	1.3m	1.3m	5.4m
19-H_2	1.3m	2.0m	2.07m	1.3m	1.3m	2.0m
20-H_3	0.86t(6.3)	0.95t(7.5)	0.95t(7.5)	0.87t(6)	0.87t(6.1)	0.94t(7.5)
OMe	3.64s	3.64s	3.64s	3.64s	3.64s	3.65s
OAc	2.11s	2.10s	2.10s	2.10s	2.10s	2.08s
OAc	2.09s	2.03s	2.02s	2.03s	2.02s	2.03s
OAc	2.06s		2.00s			2.00s
OH_b		3.5s		2.79s		3.67s

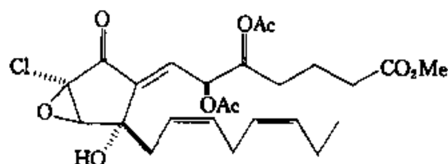




509. R = H
510. R = Ac
511. R = H, 17, 18-二氢
512. R = Ac, 17, 18-二氢

513. R = H
514. R = Ac
515. R = H, 17, 18-二氢
516. R = Ac, 17, 18-二氢



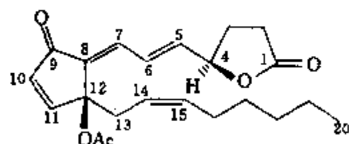


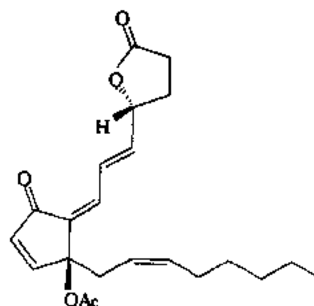
517. R = H
518. R = Ac
519. R = H, 17, 18-二氢
520. R = Ac, 17, 18-二氢

521

表 11-48 前列腺素类化合物 522,523 的 ^{1}H-NMR 化学位移[111]

化合物 / 质子	522	523	化合物 / 质子	522	523
2-H	2.55m	2.58dd(6.9,9.3)	13-H	2.71br dd(8.1,14.2)	2.65br dd(7.6,14.3)
3-H	2.04m	2.05m		2.91br dd(7.1,14.2)	2.84br dd(7.3,14.3)
	2.52m	2.47m	14-H	5.15m	5.22m
4-H	5.15m	5.10br dd(7.3,7.9)	15-H	5.52m	5.54m
5-H	6.17dd(4.9,14.7)	6.08dd(7.3,15.6)	16-H	1.94br q(6.3)	1.97br q(7.2)
6-H	6.82ddd(1.5,12.0,14.7)	7.82br dd(11.3,15.6)	17～19-H	1.20～1.34m	1.22～1.33m
7-H	6.91br d(12.0)	6.53d(11.3)	20-H	0.87t(7.2)	0.88t(7.1)
10-H	6.42d(6.1)	6.38d(6.1)	CH_3CO	2.02s	2.03s
11-H	7.50br d(6.1)	7.49d(6.1)			





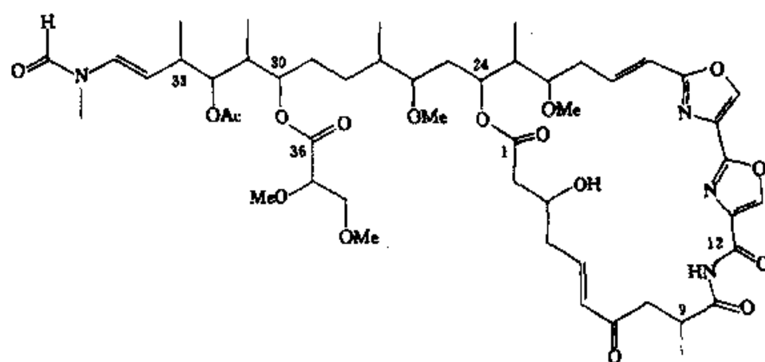
522

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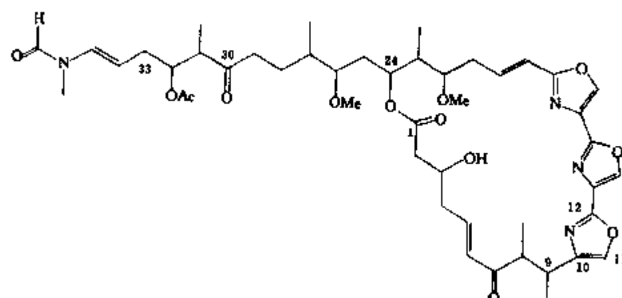
二、大环内酯类化合物的¹H-NMR 化学位移

表 11-49 大环内酯化合物 524,525 的¹H-NMR 化学位移[112]

质子＼化合物	524	525	质子＼化合物	524	525
1-H			24-H	5.23m	5.22m
2-H	2.45m	2.46m	25-H	1.42m	1.55m
	2.48m	2.54m		1.54m	1.60m
3-H	4.27m	4.38m	26-H	2.91m	2.96m
4-H	2.39m	2.40m	26-OMe	3.27s	3.28s
	2.42m	2.52m	27-H	1.72m	1.60m
5-H	7.08dt(15.6,7.3)	7.18dd(16.1,7.2)	27-Me	0.81d(6.8)	0.82d(6.8)
6-H	6.26br d(15.6)	6.08br d(16.1)	28-H	1.42m	1.24m
7-H					1.80m
8-H	2.67m	2.54m	29-H	1.54m	2.48m
	2.71m		30-H	5.09m	
8-Me		1.03d(6.8)	31-H	1.80m	2.75m
9-H	3.05m	3.37m	31-Me	0.99d(6.8)	1.06d(6.8)
9-Me	1.23d(6.8)	1.31d(6.8)	32-H	4.75m	5.12dd(8.8,4.1)
10-H			32-OAc		
11-H		7.42s		2.06s	1.99s
12-H			33-H	2.50m	2.46m
13-H			33-Me	0.95d(6.8)	
14-H	8.33s	8.04s	34-H	4.94(4.96)dd,	4.95(4.98)dd,
15-H				14.1,9.3	14.2,9.1
16-H			35-H	6.48(7.13)d(14.1)	6.48(7.12)d,14.2
17-H	8.10s	8.03s	35-NMe	2.99(3.03)s	3.01(3.05)s
18-H			35-NCHO	8.27(8.05)s	8.27(8.06)s
19-H	6.42dd(16.1,3.5)	6.35br d(15.6)	36-H		
20-H	6.95dt(16.1,7.3)	7.06m	37-H	3.90m	
21-H	2.44m	2.42m	37-OMe	3.46s	
	2.67m	2.65m	38-H	3.60m	
22-H	3.29m	3.62m		3.62m	
22-OMe	3.32s	3.32s	38-OMe	3.37s	
23-H	1.72m	1.92m	NH	10.19br s	
23-Me	0.85d(7.3)	0.94d(6.8)			



524



525

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第三篇　^{13}C 核磁共振谱的化学位移和偶合常数

第十二章　烃类化合物的^{13}C-NMR 化学位移

烃类化合物的^{13}C-NMR 谱化学位移主要特点：

(1) 烷烃的^{13}C-NMR 谱中化学位移具有加和性，饱和烃类各碳的化学位移可根据规则计算。

(2) 取代基直接结合的碳化学位移移向低场，位移的大小与取代基的电负性有关，一般情况下 $H < CH_3 < SH < NH_2 < OH < Br < Cl < F$；取代基使 β 位碳化学位移移向低场；使 γ 位碳移向高场。

(3) 取代环己烷的^{13}C-NMR 的化学位移，如果取代基为 a 键，则使 γ-C 向高场位移。

(4) 烯烃的化学位移比相应烷烃碳低 80 ~ 160，末端烯碳比连接有烷基的烯碳处于高场，相差大约为 10 ~ 40；与双键连接的 β，γ，δ 碳与相应的烷烃比较化学位移很相近。

(5) 芳香烃的化学位移随取代基的不同而异，取代基对 C-1 的化学位移影响最大为 ± 35 左右化学位移单位，对于邻位及对位碳影响为 ± 15 化学位移单位，对间位碳影响较小。

第一节　链烷烃的^{13}C-NMR 化学位移及其计算

一、链烷烃的^{13}C-NMR 化学位移

CH_4　−2.3

CH_3　7.3
|
CH_3

CH_3　15.4
|
CH_2　15.9
|
CH_3

CH_3　13.0
|
CH_2　24.8
|
CH_2
|
CH_3

CH_3　24.1
|
CH　25.0
|
$(CH_3)_2$

CH_3　14.2
|
CH_2　22.8
|
CH_2　34.8
|
CH_2
|
CH_3

CH_3　11.8
CH_2　32.0
CH　30.1
$(CH_3)_2$　22.3

CH_3　31.3
|
C　27.7
|
$(CH_3)_3$

CH_3　14.2
|
CH_2　23.1
|
CH_2　32.2
|
CH_2
|
CH_2
|
CH_3

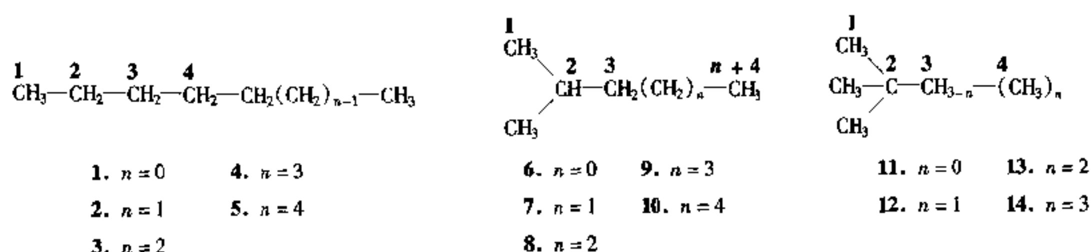
CH_3　14.1
|
CH_2　23.1
|
CH_2　32.4
|
CH_2　29.5
|
CH_2
|
CH_2
|
CH_3

CH_3　14.1
|
CH_2　22.8
|
CH_2　32.1
|
CH_2　29.5
|
CH_2
|
CH_2
|
CH_2
|
CH_3

表 12-1　链烷烃化合物 1～14 的^{13}C-NMR 化学位移数据[1]①

碳数 \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	13.5	13.7	13.7	13.6	13.8	21.9	22.7	22.4	22.4	22.3	31.6	28.7	27.0	25.6
2	22.2	22.7	22.6	22.7	22.7	29.9	27.9	28.1	28.1	28.0	28.0	30.3	32.7	35.0
3	34.1	31.7	32.0	32.1	32.0	31.6	41.9	38.9	39.3	39.2		36.5	37.9	
4			29.0	29.4	29.4	11.5	20.8	29.7	27.2	27.4		8.5	17.7	
5					29.6		14.3	23.0	32.4	29.7				
6								13.6	22.8	32.0				
7									13.8	22.7				
8										13.6				

① 二氧六环中测定。



二、取代正辛烷的^{13}C-NMR 化学位移

表 12-2　取代正辛烷的^{13}C-NMR 化学位移数据

取代基 X	X—CH_2	—CH_2	—CH_2	—CH_2	—CH_2	—CH_2	—CH_2	—CH_3
—H	14.1	22.8	32.1	29.5	29.5	32.1	22.8	14.1
—CH=CH_2	34.5	～29.6	～29.6	～29.6	～29.6	32.2	23.0	13.9
—C_6H_5	36.2	31.7	～29.6	～29.6	～29.6	32.1	22.8	14.1
—F	84.2	30.6	25.3	29.3	29.3	31.9	22.7	14.1
—Cl	45.1	32.8	27.0	29.0	29.2	31.9	22.8	14.1
—Br	33.8	33.0	28.3	28.8	29.2	31.8	22.7	14.1
—I	6.9	33.7	30.6	28.6	29.1	31.8	22.6	14.1
—OH	63.1	32.9	25.9	29.5	29.4	31.9	22.8	14.1
—OC_8H_{17}	71.1	30.0	26.3	29.6	29.4	32.0	22.8	14.1
—ONO	68.3	29.2	26.0	29.3	29.3	31.9	22.7	14.0
—NH_2	42.4	34.1	27.0	29.5	29.4	31.9	22.7	14.1
—NO_2	75.8	26.2	27.9	～29.6	～29.6	31.4	22.6	14.0
—SH	24.7	34.2	28.5	29.2	29.1	31.9	22.7	14.1
—SCH_3	34.5	29.0	29.4	29.4	29.4	31.9	22.8	14.1
—SOC_8H_{17}	52.6	～29.1	～29.1	～29.1	～29.1	31.8	22.7	14.1
—CHO	44.0	22.2	～29.3	～29.3	～29.3	31.9	22.7	14.1
—$COCH_3$	43.7	24.1	～29.5	～29.5	～29.5	32.0	22.8	14.1
—COOH	34.2	24.8	～29.3	～29.3	～29.3	31.9	22.7	14.1
—$COOCH_3$	34.2	25.1	29.3	29.3	29.3	31.9	22.8	14.1
—COCl	47.2	25.1	28.5	29.1	29.1	31.8	22.7	14.1
—CN	17.2	25.5	～29.9	～29.9	～29.9	31.8	22.7	14.0

三、烷烃的^{13}C-NMR 化学位移的计算经验式

$$\delta = -2.3 + \sum_i Z_i + s + \sum_j k_j \tag{12-1}$$

式中　δ——以 TMS 为内部标准的化学位移值；

Z_i——取代基增值（见表 12-3）；

s——邻碳的位阻增值（见表 12-4）；

k——γ 取代基构象角度增值（见表 12-5）。

表 12-3　取代基增值 Z_i①

取代基＼取代基位置		α	β	γ	δ	取代基＼取代基位置		α	β	γ	δ
—H		0.0	0.0	0.0	0.0	—NC		31.5	7.6	−3.0	0.0
—C<	(★)	9.1	9.4	−2.5	0.3	—S—	(★)	10.6	11.4	−3.6	−0.4
—C—C—(O)	(★)	21.4	2.8	−2.5	0.3	—S—CO—		17.0	6.5	−3.1	0.0
						—SO—	(★)	31.1	9.0	−3.5	0.0
—C=C—	(★)	19.5	6.9	−2.1	0.4	—SO_2Cl		54.5	3.4	−3.0	0.0
—C≡C—		4.4	5.6	−3.4	−0.6	—SCN		23.0	9.7	−3.0	0.0
—Ph		22.1	9.3	−2.6	0.3	—CHO		29.9	−0.6	−2.7	0.0
—F		70.1	7.8	−6.8	0.0	—CO—		22.5	3.0	−3.0	0.0
—Cl		31.0	10.0	−5.1	−0.5	—COOH		20.1	2.0	−2.8	0.0
—Br		18.9	11.0	−3.8	−0.7	—COO^-		24.5	3.5	−2.5	0.0
—I		−7.2	10.9	−1.5	−0.9	—COO—		22.6	2.0	−2.8	0.0
—O—	(★)	49.0	10.1	−6.2	0.0	—CON<		22.0	2.6	−3.2	−0.4
—O—CO—		56.5	6.5	−6.0	0.0	—COCl		33.1	2.3	−3.6	0.0
—O—NO		54.3	6.1	−6.5	−0.5	—CS—N<		33.1	7.7	−2.5	0.6
—N<	(★)	28.3	11.3	−5.1	0.0	—C=NOH		11.7	0.6	−1.8	0.0
—N^+<	(★)	30.7	5.4	−7.2	−1.4	—C=NOH		16.1	4.3	−1.5	0.0
—NH_3^+		26.0	7.5	−4.6	0.0	—CN		3.1	2.4	−3.3	−0.5
—NO_2		61.6	3.1	−4.6	−1.0	—Sn<		−5.2	4.0	−0.3	0.0

① 表 12-3 中代“★”的取代基的位阻不计。

表 12-4　邻碳的位阻增值

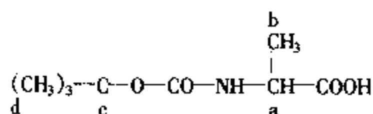
计算的碳原子	邻碳的位阻增值				计算的碳原子	邻碳的位阻增值			
	伯	仲	叔	季		伯	仲	叔	季
伯　碳	0.0	0.0	−1.1	−3.4	叔　碳	0.0	−3.7	−9.5	−15.0
仲　碳	0.0	0.0	−2.5	−7.5	季　碳	−1.5	−8.4	−15.0	−25.0

表 12-5　γ 取代基的构象角度增值

构　象	K	构　象	K
重叠式（^{13}CX）	−4.0	反折式（^{13}C, X）	0.0
顺折式（^{13}C, X）	−1.0	反　式（^{13}C, X）	2.0
		不定形	0.0

以（12-1）式算出的烷烃的化学位移计算值和实测值相差在5ppm以内，但是有的情况下却相差甚大，因而不能用此式计算。

举例：



(a)		(b)	
基本值	-2.3	基本值	-2.3
1αC	9.1	1αC	9.1
1αCOOH	20.1	1βCOOH	2.0
1αNH	28.3	1βNH	11.3
1βCOO	2.0	1γCOO	-2.8
1δC	0.3	S (p, 3)	-1.1
S (t, 2)	-3.7	计算值	16.2
计算值	53.8	实测值	17.3
实测值	49.0		

(c)		(d)	
基本值	-2.3	基本值	-2.3
3αC	27.3	1αC	9.1
1αOCO	56.5	2βC	18.8
1γNH	-5.1	1βOCO	6.5
1δC	0.3	1δNH	0.0
S (q, 1)	-1.5	S (p, 4)	-3.4
计算值	75.2	计算值	28.7
实测值	78.1	实测值	28.1

四、各种甲基的^{13}C-NMR化学位移

表 12-6　甲基的^{13}C-NMR化学位移数据

取代基X	δ_{CH_3-X}	取代基X	δ_{CH_3-X}	取代基X	δ_{CH_3-X}
—H	-2.3	4-吡啶	20.6	—OCH_2CH_3	58.8
—CH_3	8.4	2-联呋喃甲酰	13.7	—$OCH(CH_3)_2$	56.1
—CH_2CH_3	15.4	1-吡咯	35.9	—O—环己烷基	55.1
—$CH(CH_3)_2$	24.1	2-吡咯	11.8	—O—苯	54.0
$C(CH_3)_3$	31.3	1-吡唑	38.4	—O—COC_8H_{17}	51.4
—$(CH_2)_6CH_3$	14.1	—SC_8H_{17}	15.5	—OCO—环己烷基	51.0
—苄基	15.7	—S—C_6H_5	15.6	—$OCOCH{=}CH_2$	50.9
—CH_2F	14.4	—SO—CH_3	43.3	—NH_2	26.9
—CH_2Cl	17.7	—CHO	31.2	—$N(CH_3)_2$	47.5
—CH_2Br	20.2	—$COCH_3$	28.1	—NH—环己烷基	33.5
—CH_2I	23.0	—CO—环已烯基	27.6	—NH—苯基	30.2
—CH_2OH	18.8	1-吲哚	32.1	—$N(CH_3)C_6H_5$	39.9
—$CH_2OCOC_8H_{17}$	14.3	2-吲哚	13.4	—$N(CH_3)CHO$	36.2; 31.1
—CH_2OCH_3	15.9	3-吲哚	9.8	—NO_2	57.1
—CH_2CHO	5.2	4-吲哚	21.6	—NC	26.8
—CH_2COCH_3	7.3	5-吲哚	21.5	—SCH_3	19.3
—CH_2COOH	9.0	6-吲哚	21.7	—COC_6H_5	24.9
环戊烷基	20.5	7-吲哚	16.6	—COOH	21.1
环已烷基	23.1	—F	75.2	—$COOCH_3$	20.0
苯基	21.4	—Cl	24.9	—$COSC_4H_9$	30.1
α-萘	19.1	—Br	10.0	—$CON(C_4H_9)_2$	21.4
β-萘	21.5	—I	-20.7	—CN	1.3
2-吡啶	24.2	—OH	50.2		
3-吡啶	18.0	—OCH_3	60.9		

第二节　环烷烃的^{13}C-NMR化学位移

一、环烷烃的^{13}C-NMR化学位移

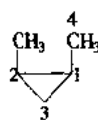
$(CH_2)_n$	n	δ	n	δ	n	δ
	3	−2.8	10	25.1	18	27.5
	4	22.9	11	26.3	20	28.0
	5	25.6	12	23.8	30	29.3
	6	27.1	13	26.2	40	29.4
	7	28.8	14	25.2	72	29.7
	8	26.8	15	27.0		
	9	26.0	16	26.9		

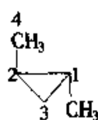
二、取代的三元环烷烃的^{13}C-NMR化学位移

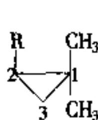
表 12-7　取代三元环烷烃的^{13}C-NMR化学位移数据[2~4]①

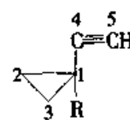
碳数＼化合物	1	2	3	4	5	6	7	8	9	10	11	12	13
1	9.8	14.2	11.5	17.2	−0.5	6.7	8.0	9.3	4.0	17.87	62.13	15.17	22.45
2	9.8	14.2	14.1	29.8	8.1	16.1	24.4	13.2	14.4	17.05	15.72	18.87	15.35
3	13.6	14.6	14.1	23.3	8.1	16.1		182.0	67.5	21.30	20.87	23.78	22.15
4	13.0	19.0	25.7	22.7	87.5	90.2				174.32	172.49	171.46	171.65
5				24.8	64.0	64.0				60.19	60.49	61.10	61.10
6						24.0				14.26	14.26	14.20	14.20

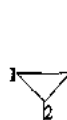
① 在 C_6D_6 中测定。

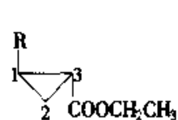

1


2


3. R = H
4. R = Br

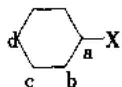

5. R = H
6. R = CH_3


7. R = NH_2
8. R = COOH
9. R = CH_2OH


10. R = CH_3
11. R = OCH_3
12. R = Br
13. R = $COOCH_3$

三、单取代环己烷的^{13}C-NMR化学位移

表 12-8　单取代环己烷的^{13}C-NMR化学位移数据



取代基X＼取代位置	a	b	c	d	取代基X＼取代位置	a	b	c	d
—H	27.6	27.6	27.6	27.6	—Cl	59.8	37.2	25.2	25.6
—CH_3	33.4	36.0	27.1	27.0	—Br	52.6	37.9	26.1	25.6
—CH_2CH_3	40.2	33.7	27.1	27.4	—I	31.8	39.8	27.4	25.5
—$CH_2CH_2CH_2CH_3$	38.4	34.1	27.1	27.3	—OH	70.0	36.0	25.0	26.4
—$C(CH_3)_3$	48.8	28.1	27.7	27.1	—OCH_3	78.6	32.3	24.3	26.7
—环己基	44.3	30.8	27.4	27.4	—$OCOCH_3$	72.3	32.2	24.4	26.1
—C_6H_5	45.1	34.9	27.4	26.7	—NH_2	51.1	37.7	25.8	26.5
—F	90.5	33.1	23.5	26.0	—$NH_3^+Cl^-$	51.5	33.4	25.6	26.0

续表

取代位置 / 取代基 X	a	b	c	d	取代位置 / 取代基 X	a	b	c	d
—N═C═N—	55.7	35.0	24.7	25.5	—COO⁻	47.2	30.9	26.9	26.9
$—NO_2$	84.6	31.4	24.7	25.5	$—COOCH_3$	43.4	29.6	26.0	26.4
—SH	38.5	38.5	26.8	25.9	—COCl	55.4	29.7	25.5	25.9
$—COCH_3$	51.5	29.0	26.6	26.3	—CN	28.3	30.1	24.6	25.8
—COOH	43.7	29.6	26.2	26.6					

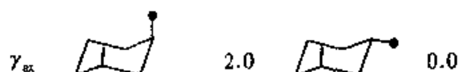
四、取代环己烷的化学位移的计算

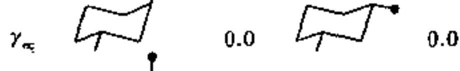
1. 甲基取代的环己烷中取代甲基的加和值

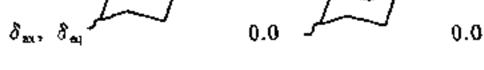
基本值

 18.8  23.1

甲基取代位置

α  6.4  10.4 γ_{ax}  2.0  0.0

β_{eq}  −6.8  −2.8 γ_{eq}  0.0  0.0

β_{ax}  −2.8  −2.8 δ_{ax}, δ_{eq}  0.0  0.0

2. 甲基取代的环己烷中环碳的^{13}C-NMR 化学位移计算中的加和值

基本值 27.1

取代位置

α_{eq}  6.0 α_{ax}  1.4

β_{eq}  9.0 β_{ax}  5.4

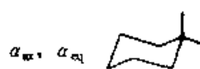
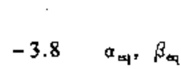
γ_{eq}  0.0 γ_{ax}  −6.4

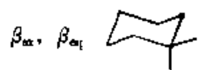
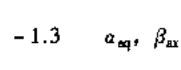
δ_{eq}  −0.2 δ_{ax}  −0.1

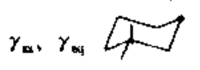
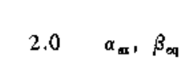
3. 二取代修正值

基本值 27.1

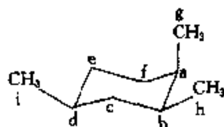
同碳二取代 邻碳二取代

α_{ax}, α_{eq}  −3.8 α_{eq}, β_{eq}  −2.5 β_{eq}, γ_{ax}  −0.8

β_{ax}, β_{eq}  −1.3 α_{eq}, β_{ax}  −2.9 β_{ax}, γ_{eq}  1.6

γ_{ax}, γ_{eq}  2.0 α_{ax}, β_{eq}  −3.4

4. 举例



(a) 基本值	27.1
$1\alpha_{ax}$	1.4
$1\beta_{eq}$	9.0
$1\delta_{eq}$	-0.2
$1\alpha_{ax}, \beta_{eq}$	-3.4
计算值	33.9
实测值	33.7(34.1)

(b) 基本值	27.1
$1\alpha_{eq}$	6.0
$1\beta_{ax}$	5.4
$1\gamma_{eq}$	0.0
$1\alpha_{eq}, \beta_{ax}$	-2.9
计算值	35.6
实测值	35.5

(c) 基本值	27.1
$2\beta_{eq}$	18.0
$1\gamma_{ax}$	-6.4
$1\beta_{eq}, \gamma_{ax}$	-0.8
计算值	37.9
实测值	38.0

(d) 基本值	27.1
$1\alpha_{eq}$	6.0
$1\gamma_{eq}$	0.0
$1\delta_{ax}$	-0.1
计算值	33.0
实测值	32.9

(e) 基本值	27.1
$1\beta_{eq}$	9.0
$1\gamma_{ax}$	-6.4
$1\delta_{eq}$	-0.2
计算值	29.5
实测值	29.3

(f) 基本值	27.1
$1\beta_{ax}$	5.4
$2\gamma_{eq}$	0.0
$1\beta_{ax}, \gamma_{eq}$	1.6
计算值	34.1
实测值	33.7(34.1)

(g) 基本值	18.8
$1CH_3\beta_{eq}$	-6.8
$1CH_3\delta_{eq}$	0.0
计算值	12.0
实测值	11.7

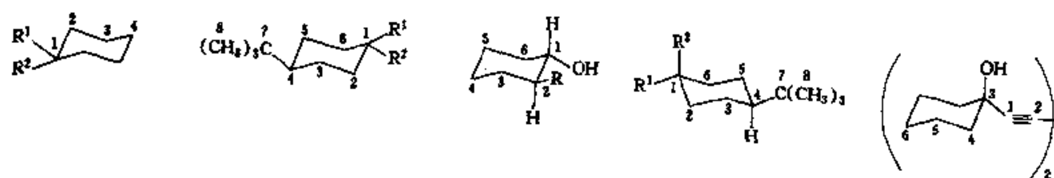
(h) 基本值	23.1
$1CH_3\beta_{ax}$	-2.8
$1CH_3\gamma_{eq}$	0.0
计算值	20.3
实测值	20.3

(i) 基本值	23.1
$1CH_3\gamma_{eq}$	0.0
$1CH_3\delta_{ax}$	0.0
计算值	23.1
实测值	23.0

五、几个取代环己烷的^{13}C-NMR 化学位移

表 12-9 取代环己烷 14～25 的^{13}C-NMR 化学位移数据[5～9]

C \ 化合物	14	15	16	17	18	19	20	21	22	23	24	25
1	79.46	74.71	29.04	27.73	26.61	26.18	26.16	76.4	75.7	65.0	70.4	83.1
2	32.15	29.41	30.47	26.73	27.09	27.00	26.93	40.3	75.7	33.3	35.7	68.2
3	24.86	20.43	25.73	23.13	27.44	27.44	27.32	33.8	33.0	21.0	25.7	68.4
4	25.90	26.29	25.73	26.25	48.01	48.01	47.94	25.8	24.5	48.2	47.3	39.8
5								25.3	24.5			23.4
6								35.6	33.0			25.4
7					27.30	27.30	27.27			32.4	32.1	
8					32.26	32.26	32.24			27.4	27.5	
R	55.05	55.05						18.7				



14. $R^1 = OCH_3$　**18.** $R^1 = R^2 = H$

15. $R^1 = H$, $R^2 = OCH_3$　**19.** $R^1 = H$, $R^2 = D$　**21.** $R = CH_3$　**23.** $R^1 = H$, $R^2 = OH$

16. $R^1 = CN$, $R^2 = H$　**20.** $R^1 = D$, $R^2 = H$　**22.** $R = OH$　**24.** $R^1 = OH$, $R^2 = H$　**25**

17. $R^1 = H$, $R^2 = CN$

第三节　并合的环烷烃的^{13}C-NMR 化学位移

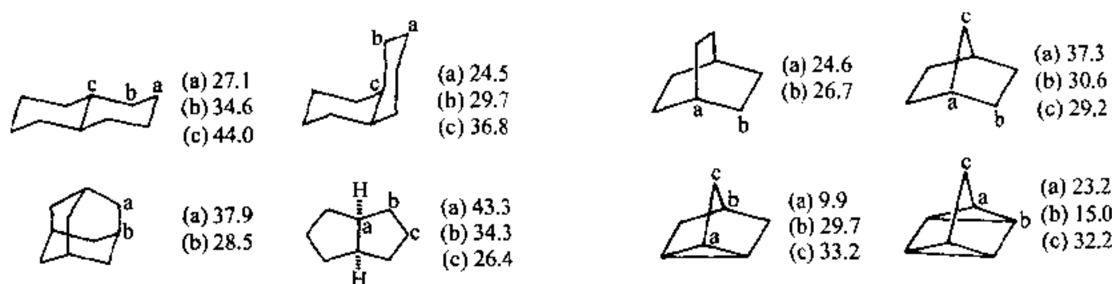
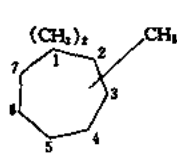


表 12-10　并环烷烃 1～8 的^{13}C-NMR 化学位移数据[10～12]

C \ 化合物①	1	2	3	4	5	6	7	8
1	35.9	32.7	33.6	71.72	47.45	434	90.9	60.9
2	43.5	51.7	40.9	79.70	34.43	34.3	42.2	41.1
3	32.7	29.8	32.3	43.23	80.34	26.4	26.1	26.0
4	30.0	39.7	37.2	62.18	69.41		33.7	34.1
5	30.7	30.4	40.3	37.21	26.76		52.0	50.9
6	23.1	23.8	22.8	26.46	20.23			
7	44.2	42.8	42.9	56.60	56.51			
R					176.03			

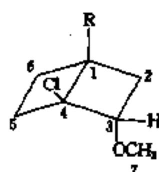
① 化合物 1～3 在 CS_2 中测定。



1. 2-CH_3

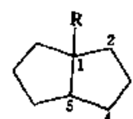
2. 3-CH_3

3. 4-CH_3



4. $R = Cl$

5. $R = COOH$



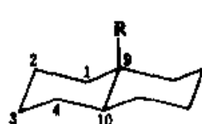
6. $R = H$

7. $R = OH$

8. $R = SCH_3$

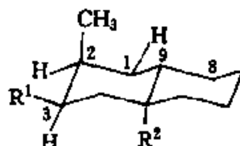
表 12-11 并环烷烃 9~14 的^{13}C-NMR 化学位移数据[13]

C \ 化合物	9	10	11	12	13	14
1	34.7	42.4	44.3	44.2	37.2	38.4
2	27.2	22.2	39.3	39.8	29.5	37.1
3	27.2	27.4	35.8		27.4	
4		29.4			25.8	
5					33.6	
6					21.9	
7					27.4	
8			31.0		20.0	31.0
9	44.2	34.8	49.4		43.0	50.6
10		46.2			38.7	
11			20.9	20.3	19.7	19.7
R		15.8	16.1	20.3		



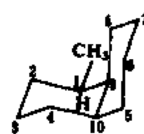
9. R = H

10. R = CH_3

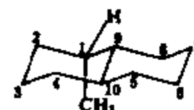


11. R^1 = H, R^2 = CH_3

12. R^1 = CH_3, R^2 = H



13



14

表 12-12 并环烷烃 15~22 的^{13}C-NMR 化学位移数据[14~18]

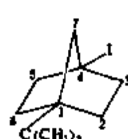
C \ 化合物	15	16	17	18	19	20	21	22
1	36.4	69.9	82.8	38.4	49.5	38.7	35.7	36.6
2	29.8	38.4	35.4	32.4	76.8	27.7	14.7	23.1
3	29.8	30.9	30.3	44.2	39.0	30.6	1.0	17.7
4	36.4	34.8	34.8	52.2	45.4			
5					28.4			
6					26.1		29.8	26.8
7	38.4	46.8	43.9	50.7	48.0	47.5		
8				31.3	18.8		26.8	53.5
9				26.6	20.3			
10					13.4			



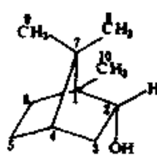
15. R = H

16. R = Cl

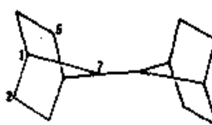
17. R = OH



18



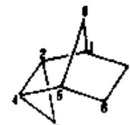
19



20



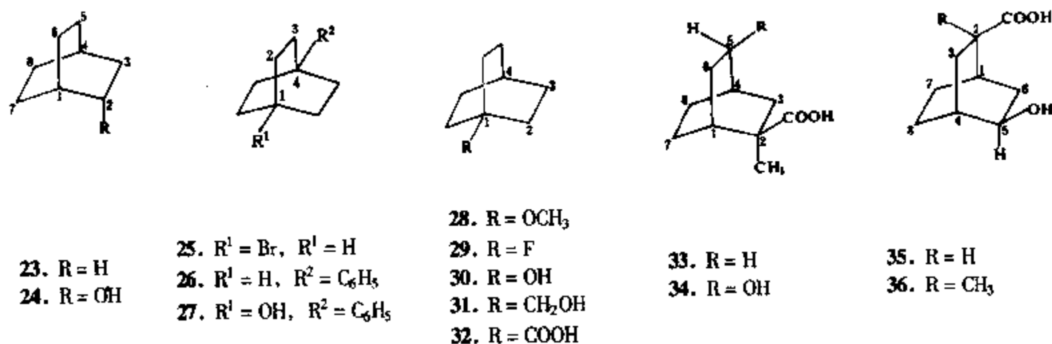
21



22

表 12-13 并环烷烃 23~36 的^{13}C-NMR 化学位移数据[19~23]

C \ 化合物	23	24	25	26	27	28	29	30	31	32	33	34	35	36
1	23.99	31.64	92.47	24.58	69.57	72.85	92.97	69.09	32.44	38.17	32.07	33.43	28.55	32.54
2		69.41	31.30	26.59	34.26	29.86	31.80	33.91	27.78	27.94	44.01	43.44	41.47	43.44
3		37.47	27.38	32.18	33.48	27.50	27.88	27.20	25.77	25.35	36.55	30.01	21.28	30.01
4	23.99	24.87	24.26	34.13	34.26	24.81	30.24	24.41	24.68	23.73	25.17	32.53	31.16	33.43
5	26.11	24.59									24.31	68.29	68.46	68.29
6	26.11	23.82									24.31	35.80	33.68	35.80
7		18.70									21.57	20.07	25.01	20.07
8		25.70									25.31	22.76	22.80	22.76
9													180.4	182.78
R									71.92	185.2				26.28



23. R = H
24. R = OH

25. R^1 = Br, R^1 = H
26. R^1 = H, R^2 = C_6H_5
27. R^1 = OH, R^2 = C_6H_5

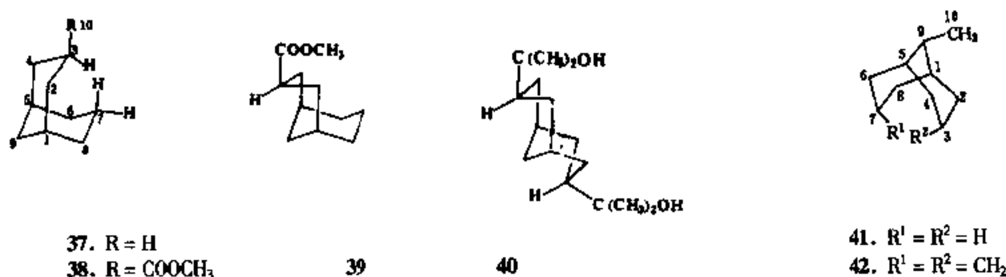
28. R = OCH_3
29. R = F
30. R = OH
31. R = CH_2OH
32. R = COOH

33. R = H
34. R = OH

35. R = H
36. R = CH_3

表 12-14　并环烷烃 37～42 的^{13}C-NMR 化学位移数据[24,25]

C \ 化合物	37	38	39	40	41	42
1	27.9	27.5	25.0	24.5	34.24	34.52
2	31.6	34.0	29.1	32.0	31.81	31.99
3	22.5	39.1	36.0	41.4	23.03	28.10
6	31.6	30.9	33.1	32.0	34.56	39.98
7	22.5	22.1	16.0	41.4	28.83	28.83
9	35.1	34.1	29.1	23.7	26.79	
10		177.1	177.2	72.7	18.84	19.11
11		51.4	51.4	27.0		
R						38.65



37. R = H
38. R = $COOCH_3$

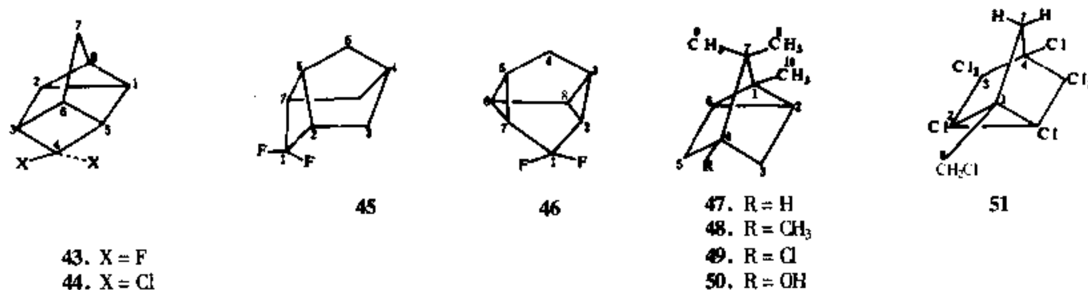
39

40

41. R^1 = R^2 = H
42. R^1 = R^2 = CH_2

表 12-15　并环烷烃 43～51 的^{13}C-NMR 化学位移数据[22,26～28]

C \ 化合物	43	44	45	46	47	48	49	50	51
1	12.91	18.95	128.10	129.02	26.3	28.8	27.5	29.8	37.9
2			49.19	28.38	20.6	20.3	19.3	19.2	61.3
3	49.19	58.20	12.91	25.22	31.3	38.2	39.3	36.1	93.1
4	128.20	91.69	25.61	25.16	41.8	43.3	69.5	79.9	76.3
5			31.77						
6	33.68	40.62	33.81	23.56					
7	31.77	34.38			43.1	44.2	45.8	43.1	41.9
8	25.61	30.65			19.4	17.7	17.6	17.3	37.9
10					9.4	11.5	12.1	12.2	
R						12.2			



45

46

47. R = H
48. R = CH_3
49. R = Cl
50. R = OH

51

43. X = F
44. X = Cl

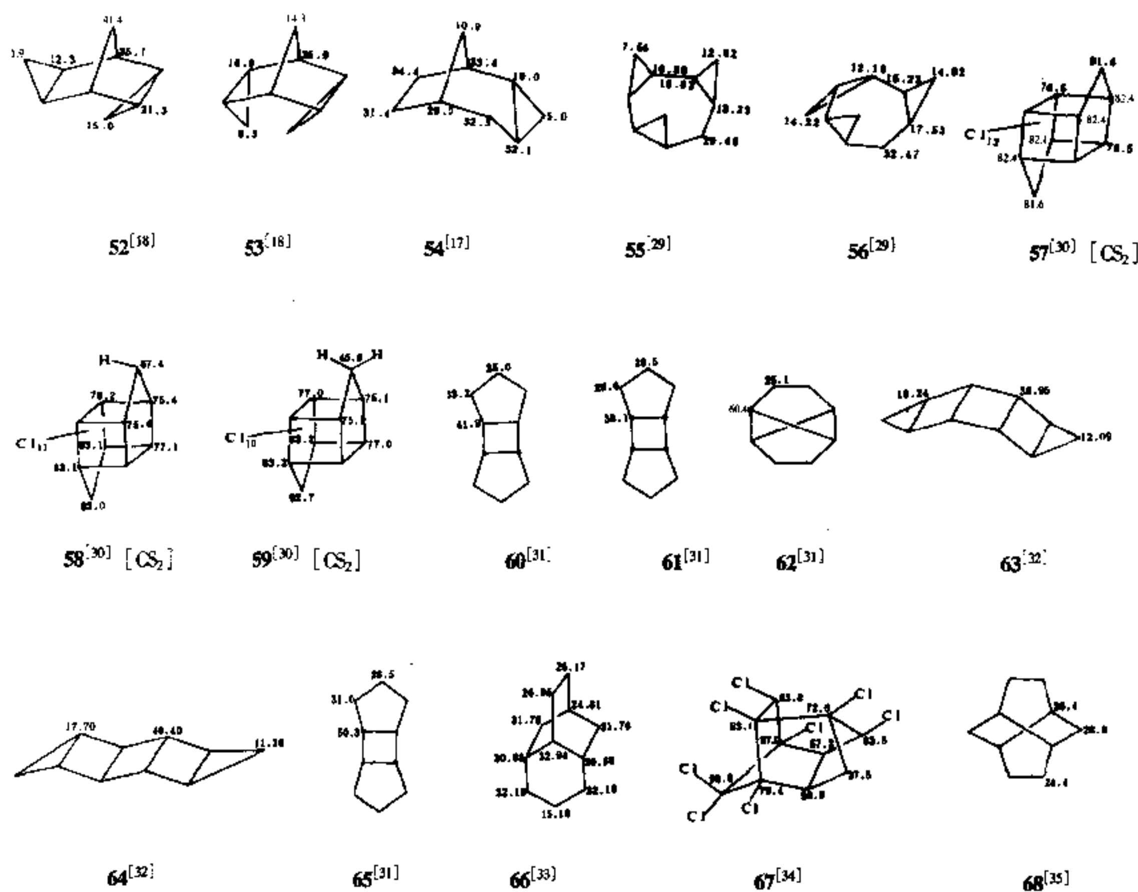
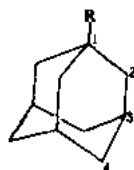


表 12-16 金刚烷类化合物 69 ~ 76 的 ^{13}C-NMR 化学位移数据[36~39]

C \ 化合物	69	70	71	72①	73	74	75	76
1	28.5	67.9	68.2	84.3	29.9	33.1	44.8	
2	37.8	45.3	47.7	40.8	44.6	102.2	100.6	59.1
3	28.5	30.8	31.7	29.8	28.9			31.1
4	37.8	36.1	35.6	35.8	36.9	33.9	34.8	36.6
5						27.3	26.4	
6						37.5	38.2	
R					31.1	46.5		

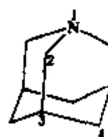
① 化合物 72 ~ 73 在 CCl_4 中测定。



69. R = H
70. R = OH
71. R = Cl
72. R = NO_2
73. R = CH_3



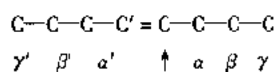
74. R = OCH_3
75. R = Cl



76

第四节　链烯化合物的^{13}C-NMR 化学位移

一、链烯化合物的^{13}C-NMR 化学位移的计算



基本值　123.3

碳取代基位置　α　10.6;　α'　−7.9

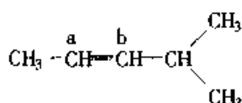
β　4.9;　β'　−1.8

γ　−1.5;　γ'　−1.5

立体校正值

对于每对顺式 α，α'-取代	−1.1
对于一对同碳 α，α-取代	−4.8
对于一对同碳 α'，α'-取代	2.5
如果一个或多个 β-取代	2.3

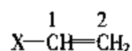
举例：



(a)	
基本值	123.3
1αc	10.3
1α′c	−7.9
2β′c	−3.6
顺式 α′，α	−1.1
计算值	121.3
实测值	121.8

(b)	
基本值	123.3
1αc	10.6
2βc	9.8
1α′c	−7.9
顺式 α，α′	−1.1
1β-取代	2.3
计算值	137.0
实测值	138.8

二、由于单取代基的影响乙烯的^{13}C-NMR 化学位移数据的加和值



$\delta_{Ci} = 123.3 + Z_i$

置换基 X	Z_1	Z_2	置换基 X	Z_1	Z_2
—H	0.0	0.0	$—OCH_3$	29.4	−38.9
$—CH_3$	10.6	−7.9	$—OCH_2CH_3$	28.5	−39.8
$—CH_2CH_3$	15.5	−9.7	$—OCH_2CH_2CH_2CH_3$	28.1	−40.4
$—CH_2CH_2CH_3$	14.0	−8.2	$—OCOCH_3$	18.4	−26.7
$—CH(CH_3)_2$	20.4	−11.5	$—N^+(CH_3)_3$	19.8	−10.6
$—CH_2CH_2CH_2CH_3$	14.6	−8.9	=N═ 吡咯烷基	6.5	−29.2
$—C(CH_3)_3$	25.3	−13.3	$—NO_2$	22.3	−0.9
$—CH_2Cl$	10.2	−6.0	—NC	−3.9	−2.7
$—CH_2Br$	10.9	−4.5	$—SCH_2—C_6H_5$	18.5	−16.4
$—CH_2I$	14.2	−4.0	$—SO_2CH=CH_2$	14.3	7.9
$—CH_2OH$	14.2	−8.4	—CHO	13.1	12.7
$—CH_2OCH_2CH_3$	12.3	−8.8	$—COCH_3$	15.0	5.8
$—CH=CH_2$	13.6	−7.0	—COOH	4.2	8.9
C_6H_5	12.5	−11.0	$—COOCH_2CH_3$	6.3	7.0
—F	24.9	−34.3	—COCl	8.1	14.0
—Cl	2.6	−6.1	—CN	−15.1	14.2
—Br	−7.9	−1.4	$—Si(CH_3)_3$	16.9	6.7
—I	−38.1	7.0	$—SiCl_3$	8.7	16.1

举例：

$$\overset{a}{Br-CH}=\overset{b}{CH}-CH_3$$

(a)			(b)		
	基本值	123.3		基本值	123.3
	Z_1（Br）	−7.9		Z_2（Br）	−1.4
	Z_2（CH_3）	−7.9		Z_1（CH_3）	10.6
	计算值	107.5		计算值	132.5
	实测值	108.9（顺式）		实测值	129.4（顺式）
		104.7（反式）			132.7（反式）

三、单烯化合物的^{13}C-NMR 化学位移

表 12-17　单烯化合物 1～12 的^{13}C-NMR 化学位移数据[40,41]①

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
1	115.95	113.49	114.66	114.17	16.80	17.34	17.51	17.69	11.42	12.01	12.29	12.45
2	133.61	140.49	138.91	138.83	125.42	123.55	124.74	124.60	124.22	122.84	123.73	123.61
3	19.41	27.39	36.68	33.86		133.21	131.54	131.82		132.43	130.64	130.97
4		13.43	22.81	31.64		25.81	35.10	32.76		20.33	29.26	26.95
5			13.75	22.49		13.62	23.07	32.44		13.79	23.04	32.33
6				13.73			13.43	22.65			13.49	22.75
7								13.90				13.89

① 化合物 1～4 在 C_6H_{14} 中测定，5～12 以纯物质测定。

$\overset{1}{CH_2}=\overset{2}{CH}-(CH_2)_n-\overset{n}{CH_3}$

1. $n=0$
2. $n=1$
3. $n=2$
4. $n=3$

$\overset{1}{CH_3}(H)\overset{2}{C}=\overset{3}{C}(H)-(CH_2)_n-\overset{n-3}{CH_3}$（反式）

5. $n=0$
6. $n=1$
7. $n=2$
8. $n=3$

$CH_3(H)C=C(H)(CH_2)_n\overset{n-3}{CH_3}$（顺式）

9. $n=0$
10. $n=1$
11. $n=2$
12. $n=3$

表 12-18　单烯化合物 13～24 的^{13}C-NMR 化学位移数据[42～44]

C \ 化合物	13	14	15	16	17	18	19	20	21	22	23	24
1	83.7	121.5	128.6	132.1	112.7	118.5	114.6	118.0	113.4	126.4	120.2	110.7
2	152.9	113.4	136.8	127.5	140.8	134.2	137.7	129.5	132.7	136.4	140.3	141.7
3					44.4	44.6	62.6	37.4	18.5	17.3	18.5	23.6

$\overset{1}{CH_2}=\overset{2}{C}(H)R$

13. R＝OCH_3
14. R＝Br
15. R＝$COCH_3$
16. R＝COOH

$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-R$

17. R＝NH_2
18. R＝Cl
19. R＝OH
20. R＝COOH

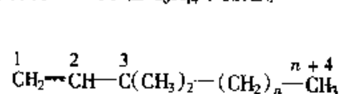
$\overset{1}{CH_2}=\overset{2}{C}(R)-\overset{3}{CH_3}$

21. R＝H
22. R＝COOH
23. R＝$CONH_2$
24. R＝CH_3

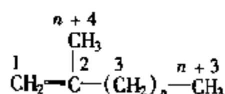
表 12-19　单烯化合物 25～33 的^{13}C-NMR 化学位移数据[40,45]①

C \ 化合物	25	26	27	28	29	30	31	32	33
1	108.50	110.68	111.26	109.06	110.16	110.07	20.38	20.55	20.56
2	149.27	148.31	141.79	146.98	145.25	145.43	123.49	123.13	123.93
3	33.78	36.90	24.20	31.09	40.46	38.01		129.58	127.97
4	29.41	35.56		12.55	21.19	30.43		27.67	36.80
5		8.96		22.55	13.63	22.83		12.75	21.63
6					22.08	13.95		19.87	14.10
7						22.26		17.86	20.19
8									18.35

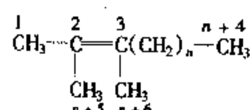
① 化合物 25～30 在 C_6H_{14} 中测定。



25. n＝0
26. n＝1

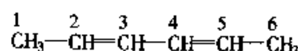


27. n＝0
28. n＝1
29. n＝2
30. n＝3

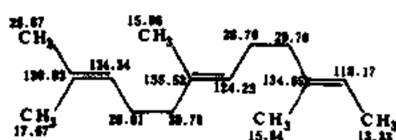


31. n＝0
32. n＝1
33. n＝2

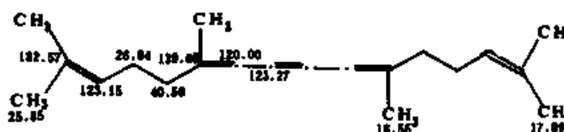
四、多烯化合物的^{13}C-NMR 化学位移



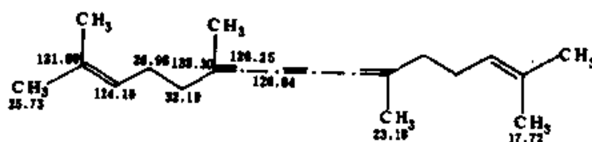
化合物 \ C	1	2	3	4	5	6	文献
34 (2E, 4E)	17.60	125.82	132.31				46
35 (2E, 4Z)	18.00	128.31	130.21	127.41	123.12	13.01	46
36 (2Z, 4Z)	12.90	124.92	125.32				46



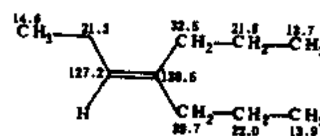
37[47]



38[48]



39[48]

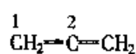


40[49]

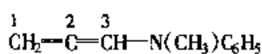
表 12-20　联烯化合物 41～51 的^{13}C-NMR 化学位移数据[50～53]①

C \ 化合物①	41	42	43	44	45	46	47	48	49	50	51
1	72.6	87	79.8	79.9	80.2	72.5	73.8	73.8	88.0	88.6	98.0
2	211.7	204	210.2	210.7	210.2	208.5	207.9	208.6	26.0	22.5	28.4
3		106	95.4	95.7	94.5	83.3	90.7	89.0	32.1	22.5	28.4
4						12.3	20.7	29.6	187.1	186.3	184.5
5							12.3	18.4	99.2	97.7	97.4
6								12.8	21.4	21.7	22.6
7									21.5	21.7	22.8

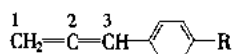
① 化合物 42 在 C_6D_6-C_6H_6 中测定。



41



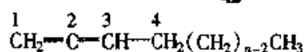
42



43. R = H

44. R = CH_3

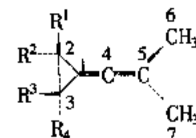
45. R = Cl



46. n = 1

47. n = 2

48. n = 3



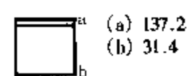
49. $R^1 = C_6H_5, R^2 = R^3 = H, R^4 = CH_3$

50. $R^1 = R^4 = CH_3, R^2 = R^3 = H$

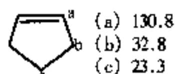
51. $R^1 = R^2 = R^3 = R^4 = CH_3$

第五节 环烯烃的^{13}C-NMR 化学位移

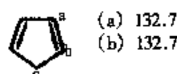
一、环烯烃的^{13}C-NMR 化学位移数据



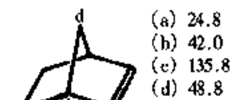
(a) 137.2
(b) 31.4



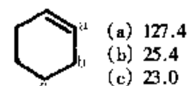
(a) 130.8
(b) 32.8
(c) 23.3



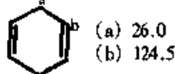
(a) 132.7
(b) 132.7



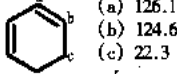
(a) 24.8
(b) 42.0
(c) 135.8
(d) 48.8



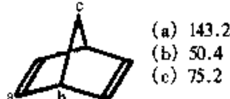
(a) 127.4
(b) 25.4
(c) 23.0



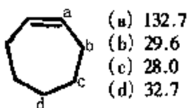
(a) 26.0
(b) 124.5



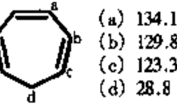
(a) 126.1
(b) 124.6
(c) 22.3



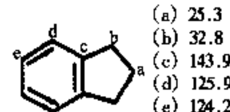
(a) 143.2
(b) 50.4
(c) 75.2



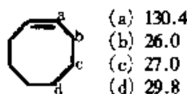
(a) 132.7
(b) 29.6
(c) 28.0
(d) 32.7



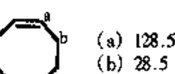
(a) 134.1
(b) 129.8
(c) 123.3
(d) 28.8



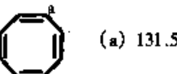
(a) 25.3
(b) 32.8
(c) 143.9
(d) 125.9
(e) 124.2



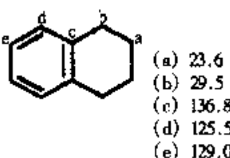
(a) 130.4
(b) 26.0
(c) 27.0
(d) 29.8



(a) 128.5
(b) 28.5



(a) 131.5

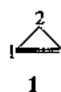


(a) 23.6
(b) 29.5
(c) 136.8
(d) 125.5
(e) 129.0

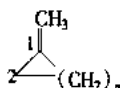
二、三元环烯烃的^{13}C-NMR 化学位移

表 12-21 三元环烯烃 1～7 的^{13}C-NMR 化学位移数据[54,55]

C \ 化合物	1	2	3	4	5	6	7
1	108.7	131.0	150.2	153.0	149.8	116.5	117.6
2	2.3	3.0	32.3	33.3	35.7	98.8	10.1
3		103.5	105.4	104.9	106.8	6.2	23.6
4						12.5	



1



2. n = 1

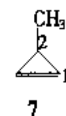
3. n = 2

4. n = 3

5. n = 4

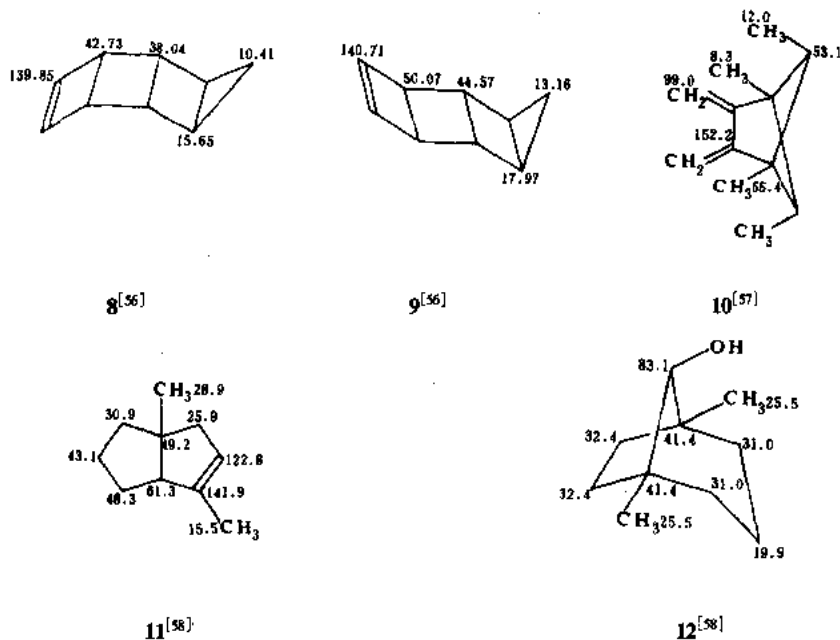


6



7

三、四元环和五元环烯烃的^{13}C-NMR 化学位移

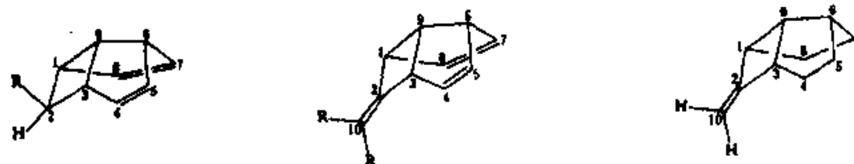


8[56]　　9[56]　　10[57]

11[58]　　12[58]

表 12-22　五元环烯烃 13～18 的^{13}C-NMR 化学位移数据[59]

C \ 化合物	13	14	15	16	17	18
1	46.57	54.83	47.11	52.77	50.84	45.56
2	28.50	57.96	48.30	149.02	131.59	161.78
4	134.03	130.20	133.06	130.78	130.89	33.40
5	138.46	140.10	139.54	137.69	137.10	32.91
6	58.71	58.28	58.66	58.05	57.57	47.53
10				106.67	123.61	106.67
R					18.07	



13, R = H
14, R = Cl
15, R = MgCl

16, R = H
17, R = CH_3

18

四、六元环烯烃的^{13}C-NMR 化学位移

表 12-23　六元环单烯 19～29 的^{13}C-NMR 化学位移数据[60,61,63,64]

C \ 化合物	19	20	21	22	23	24	25①	26	27	28	29
1	127.2	127.2	127.1	134.2	134.2	134.2	143.1	128.95	71.53	68.80	120.2
2	127.2	123.9	124.9	122.3	117.8	118.9	119.2	130.32	136.69	134.39	136.3
3	25.5	28.6	24.4	26.7	28.6	24.6	25.8	30.64	124.13	124.83	25.7
4	23.1	24.8	46.0	24.4	25.9	45.9	23.4	49.68	34.95	33.13	22.4

续表

C \ 化合物	19	20	21	22	23	24	25①	26	27	28	29
5	23.1	25.7	22.1	24.4	27.8	22.6	23.7	32.45	43.68	37.56	21.6
6	25.5	23.2	23.8	31.5	27.8	28.6	27.0	43.94	27.12	27.30	29.2
7		122.5	208.7	23.8	23.4	23.5	46.6	24.11	18.87	20.93	85.5
8					122.5	204.0	32.5	30.15	32.09	31.73	74.5
9							27.3	31.69	27.12	27.30	
10							27.0				

① 化合物25在 CCl_4 中测定。

19. R = H　**20**. R = CN　**21**. R = CHO

22. R = H　**23**. R = CN　**24**. R = CHO

25

26

27. R^1 = OH, R^2 = H

28. R^1 = H, R^2 = OH

29

五、并环烯烃的^{13}C-NMR化学位移

表 12-24　并环烯烃 30 ~ 38 的^{13}C-NMR 化学位移数据[65~69]

C \ 化合物	30	31	32	33	34	35	36	37	38
1	41.8	51.1	45.7	48.7	48.2	73.4	66.5	42.6	41.1
2	135.2	151.2	155.3	158.3	165.9	163.0	168.2	43.3	42.6
3	135.2	42.2	39.1	39.6	41.7	42.7	42.4	161.3	161.3
4	41.8	50.2	37.0	35.9	47.0	44.9	45.5	45.8	46.3
5	24.6	136.6	28.5	30.2	23.8	25.7	25.3	28.8	30.4
6	24.6	134.4	29.9	36.7	28.9	37.9	35.3	28.8	21.2
7	48.5	33.6	38.4	46.0	37.4	46.3	45.5	35.3	39.2
8			101.8	99.8	99.1	101.3	97.2	101.6	100.9
9					29.4	29.8	29.6	19.7	
10					25.8	26.3	26.3		14.6

30

31

32. R = H

33. R = CH_3

34. R = H

35. R = Cl

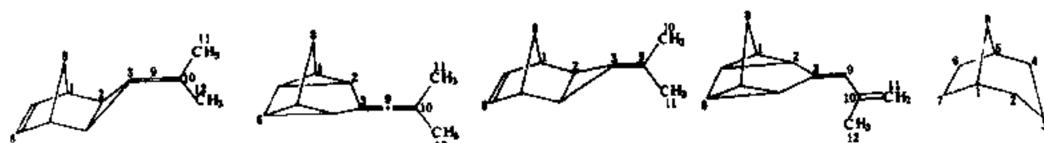
36. R = NH_2

37. R^1 = CH_3, R^2 = H

38. R^1 = H, R^2 = CH_3

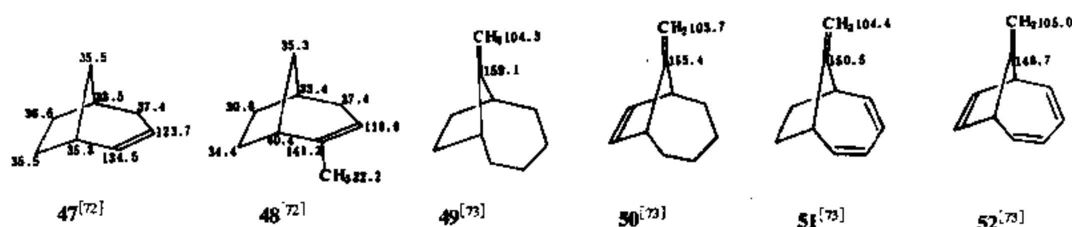
表 12-25　并环烯烃 39～46 的^{13}C-NMR 化学位移数据[70,71]

C ＼ 化合物	39	40	41	42	43	44	45	46
1	43.8	27.9	43.9		35.2	39.5	33.6	38.7
2	29.3	29.4	26.4	33.4	32.8	25.2	37.5	28.7
3	92.7	100.4	132.8	142.2	19.1	18.7	123.8	123.8
4					32.8	25.2	134.7	134.1
5					35.2	39.5	35.6	38.3
6	138.7	24.8	138.9		28.9	132.1	35.5	139.7
7					28.9	132.1	30.6	130.2
8	42.3	25.8	42.0	26.0	39.7	45.1	35.5	40.7
9	186.3	196.8	119.6	122.3				
10	97.4	96.4	21.5	142.5				
11	21.3	21.7	21.2	113.0				
12				22.9				

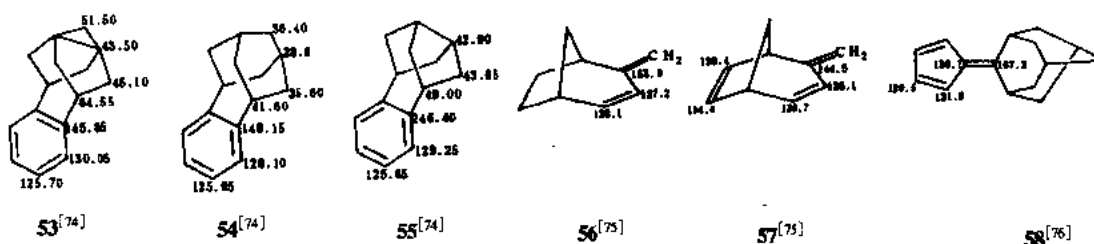


39　40　41　42

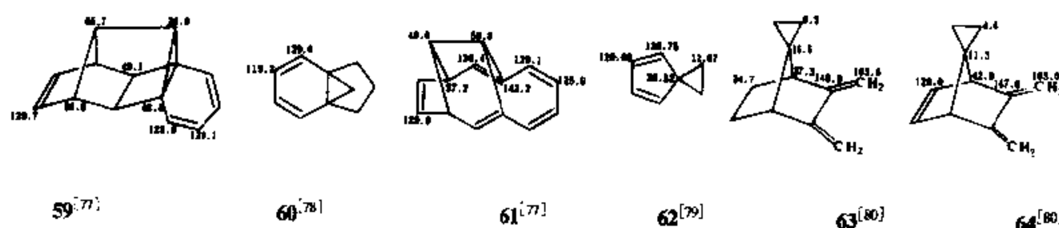
43.
44.Δ^6
45.Δ^3
46.Δ^3，Δ^6



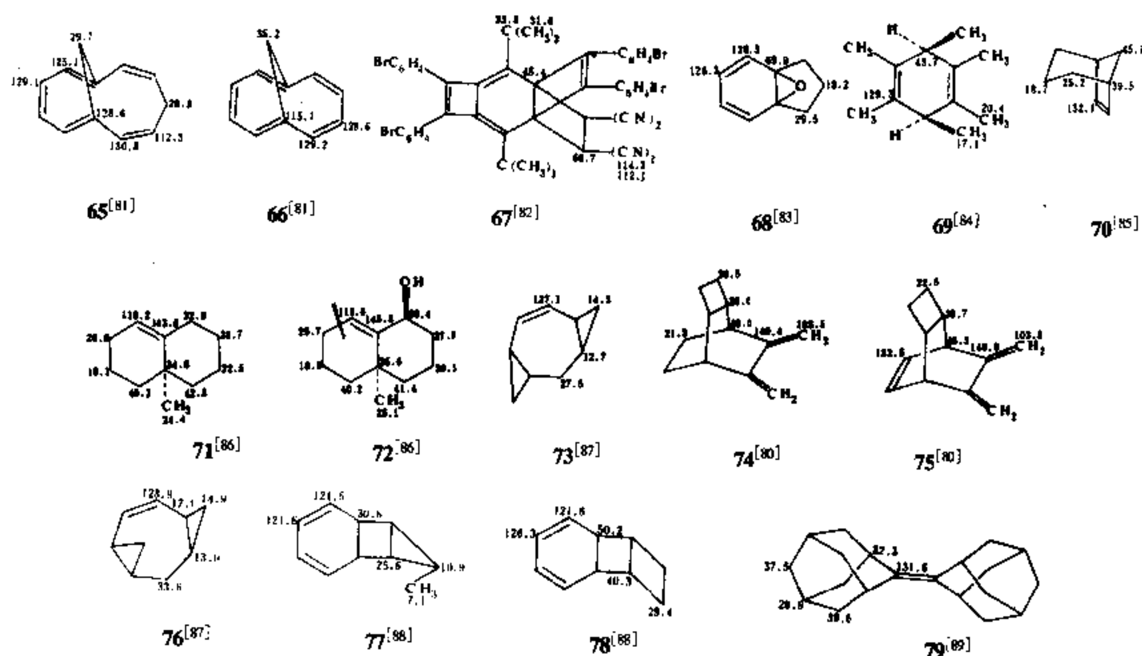
47[72]　48[72]　49[73]　50[73]　51[73]　52[73]



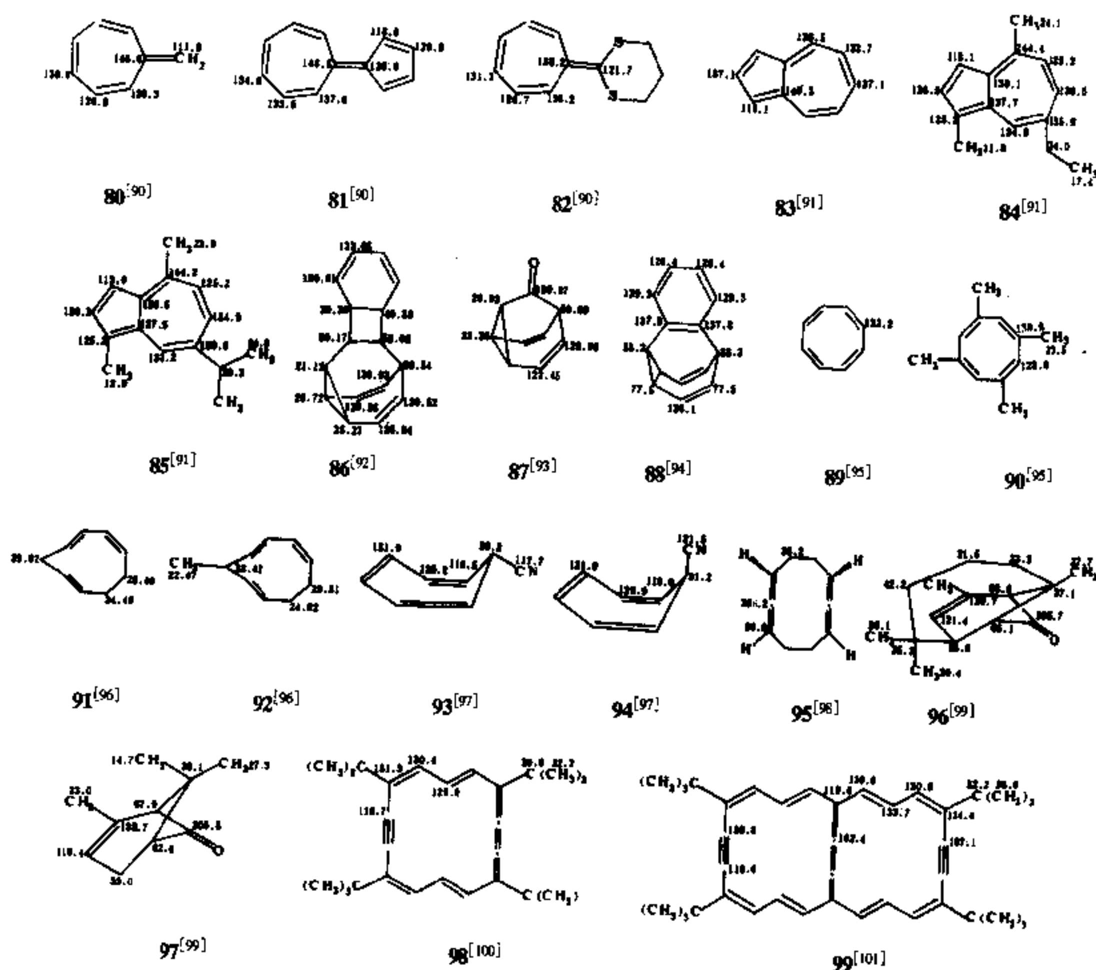
53[74]　54[74]　55[74]　56[75]　57[75]　58[76]



59[77]　60[78]　61[77]　62[79]　63[80]　64[80]



六、大环烯烃的¹³C-NMR化学位移



第六节　炔烃化合物的^{13}C-NMR 化学位移

一、取代炔烃化合物的^{13}C-NMR 化学位移

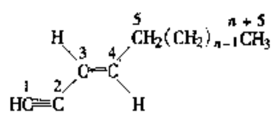
$H-\overset{a}{C}\equiv\overset{b}{C}-X$

X	a	b	X	a	b
—H	71.9	71.9	—C_6H_5	78.3	84.6
—CH_3	66.9	79.2	—OCH_2CH_3	23.2	89.4
—$CH_2CH_2CH_2CH_3$	66.0	83.0	—SCH_2CH_2	81.4	72.6
—CH_2OH	73.8	83.0			

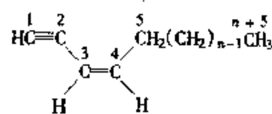
二、直链炔烃的^{13}C-NMR 化学位移

表 12-26　直链炔烃 1~11 的^{13}C-NMR 化学位移数据[9,102,104,105]

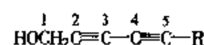
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
1	75.8	75.7	75.7	82.1	81.2	81.3	50.8	51.1	3.9	4.0	4.4
2	82.5	82.5	82.6	80.3	80.4	80.5	74.7	78.3	74.4	72.2	74.8
3	110.1	107.6	108.8	109.4	107.3	108.3	69.7	73.5	65.4	64.8	65.0
4	141.3	148.1	146.5	140.3	147.6	145.8	67.5	70.2	68.8		60.0
5	18.6	26.1	35.2	15.9	23.7	32.4	68.6	80.8	64.7		
6		12.7	21.9		13.3	22.2					
7			13.9			13.8					



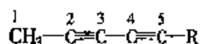
1. $n=0$
2. $n=1$
3. $n=2$



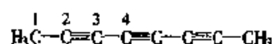
4. $n=0$
5. $n=1$
6. $n=2$



7. R = H
8. R = C_6H_5



9. R = H
10. R = CH_3

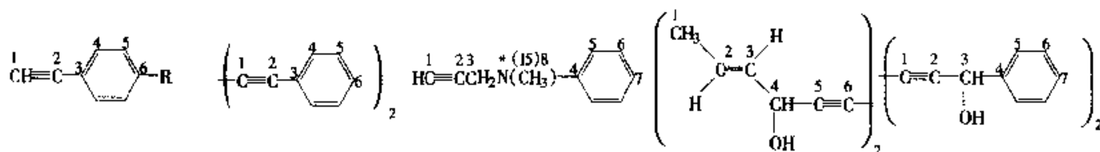


11

表 12-27　芳基炔烃 12~19 的^{13}C-NMR 化学位移数据①[9,106,107]

C \ 化合物	12	13	14	15	16	17	18	19
1	77.06	74.77	76.82	77.62	74.0	71.9	17.7	79.7
2	83.52	84.20	82.43	83.43	81.7	79.4	129.2	69.9
3	122.52	111.94	118.42	121.14	121.3	42.3	129.2	64.2
4	131.96	133.21	133.79		132.5	149.0	62.7	139.8
5	127.94	114.09	115.36		128.7	114.2	79.3	126.6
6	128.24	146.38	162.60		129.5	128.9	69.3	128.4
7						118.1		128.4
8						38.3		

① 12~15 在 CCl_4 中测定，17 在 CD_2Cl_2 中测定。

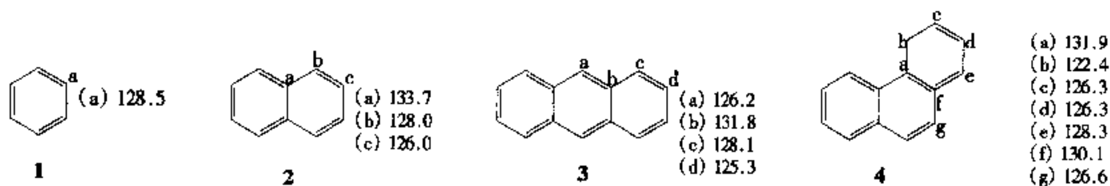


12. R = H
13. R = NH_2
14. R = F
15. R = C_6H_5

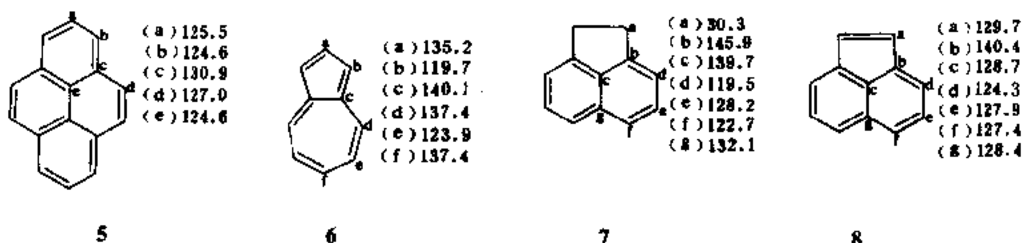
16　　17　　18　　19

第七节　芳香化合物的^{13}C-NMR 化学位移

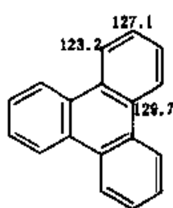
一、各种芳香化合物的^{13}C-NMR 化学位移数据

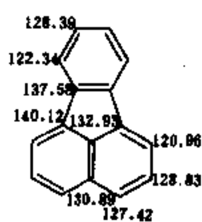


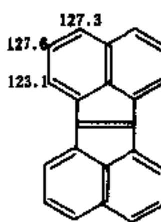
1　　2　　3　　4

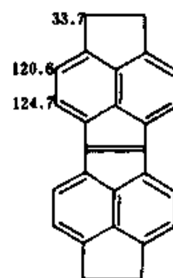


5　　6　　7　　8

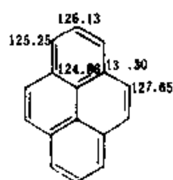


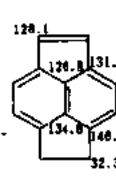


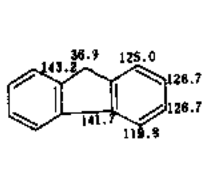


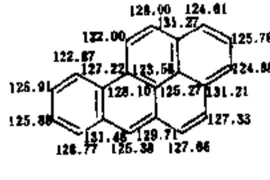


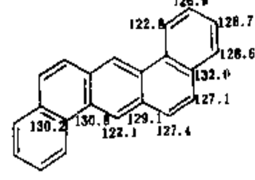
9[108]　　10[109]　　11[110]　　12[110]





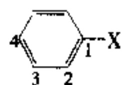






13[111]　　14[112]　　15[113]　　16[114]　　17[108]

二、单取代苯的[13]C-NMR 化学位移数据的加和值

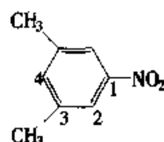


$\delta_{C_i} = 128.5 + Z_i$

取代基 X	Z_1	Z_2	Z_3	Z_4
—H	0.0	0.0	0.0	0.0
—CH_3	9.3	0.6	0.0	-3.1
—CH_2CH_3	15.7	-0.6	-0.1	-2.8
—CH $(CH_3)_2$	20.1	-2.0	0.0	-2.5
—$CH_2CH_2CH_2CH_3$	14.2	-0.2	-0.2	-2.8
—C $(CH_3)_3$	22.1	-3.4	-0.4	-3.1
—▽	15.1	-3.3	-0.6	-3.6
—CH_2Cl	2	0.0	0.2	-0.2
—CH_2Br	13	0.1	0.4	-0.3
—CF_3	9	-3.1	0.4	3.4
—CH_2OH	14	-1.4	0.0	-1.2
▽O	1	-3.1	-0.1	-0.5
—CH_2NH_2	14.9	-1.6	-0.2	-2.0
—CH_2CN	1.6	-0.7	0.5	-0.7
—CH = CH_2	7.6	-1.8	-1.8	-3.5
—C≡CH	-6.1	3.8	0.4	-0.2
—C_6H_5	13.0	-1.1	0.5	-1.0
—F	35.1	-14.3	0.9	-4.4
—Cl	6.4	0.2	1.0	-2.0
—Br	-5.4	3.3	2.2	-1.0
—I	-32.3	9.9	2.6	-0.4
—OH	26.9	-12.7	1.4	-7.3
—O^-	39.6	-8.2	1.9	-13.6
—OCH_3	30.2	-14.7	0.9	-8.1
—O—C_6H_5	29.1	-9.5	0.3	-5.3
—$OCOCH_3$	23.0	-6.4	1.3	-2.3
—NH_2	19.2	-12.4	1.3	-9.5

取代基 X	Z_1	Z_2	Z_3	Z_4
—$NHCH_3$	21.7	-16.2	0.7	-11.8
—$N(CH_3)_2$	22.4	-15.7	0.8	-11.8
—$N(CH_2CH_3)_2$	19.3	-16.5	0.6	-13.0
—$N(C_6H_5)_2$	19.3	-4.4	0.6	-5.9
—$NHCOCH_3$	11.1	-9.9	0.2	-5.6
—$NHNH_2$	22.8	-16.5	0.5	-9.6
—N = N—C_6H_5	24.0	-5.8	0.3	2.2
—N^+≡N	-12.7	6.0	5.7	16.0
—NC	-1.8	-2.2	1.4	0.9
—NCO	5.7	-3.6	1.2	-2.8
—NO	37.4	-7.7	0.8	7.0
—NO_2	19.6	-5.3	0.8	6.0
—SH	2.2	0.7	0.4	-3.1
—SCH_3	9.9	-2.0	0.1	-3.7
—$SC(CH_3)_3$	4.5	9.0	-0.3	0.0
—SO_2Cl	15.6	-1.7	1.2	6.8
—SO_3H	15.0	-2.2	1.3	3.8
—CHO	9.0	1.2	1.2	6.0
—$COCH_3$	9.3	0.2	0.2	4.2
—COOH	2.4	1.6	-0.1	4.8
—COO^-	7.6	0.8	0.0	2.8
—$COOCH_3$	2.1	1.2	0.0	4.4
—$CONH_2$	5.4	-0.3	-0.9	5.0
—COCl	4.6	2.9	0.6	7.0
—CN	-16.0	3.5	0.7	4.3
—$P(C_6H_5)_2$	8.7	5.1	-0.1	0.0
—$Si(CH_3)_3$	13.4	4.4	-1.1	-1.1

举例：



(C-1)		
	基本值	128.5
	Z_1 (NO_2)	19.6
	$2Z_3$ (CH_3)	0.0
	计算值	148.1
	实测值	148.5

(C-3)		
	基本值	128.5
	Z_1 (CH_3)	9.3
	Z_3 (CH_3)	0.0
	Z_3 (NO_2)	0.8
	计算值	138.6
	实测值	139.6

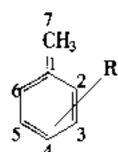
(C-2)		
	基本值	128.5
	Z_2 (NO_2)	-5.3
	Z_2 (CH_3)	0.6
	Z_4 (CH_3)	-3.1
	计算值	120.7
	实测值	121.7

(C-4)		
	基本值	128.5
	$2Z_2$ (CH_3)	1.2
	Z_4 (NO_2)	6.0
	计算值	135.7
	实测值	136.2

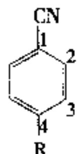
三、多取代苯的^{13}C-NMR化学位移数据

表 12-28 双取代苯 18～25 的^{13}C-NMR 化学位移数据[115-117]

C \ 化合物	18	19	20	21	22	23	24	25
1	136.4	134.5	138.9	139.1	109.6	111.0	130.3	149.8
2	136.4	129.1	129.9	116.0	132.0	133.4	129.9	127.2
3	129.9	129.1	136.8	146.5	130.0	129.7	114.7	123.6
4	126.1	134.5	127.1	112.3	143.7	139.4	159.7	147.2
5			128.8	129.2				
6			135.1	119.5				
7	19.6	20.9	21.1	21.4			33.9	63.5



18. R = *o*-CH_3
19. R = *p*-CH_3
20. R = *m*-CHO
21. R = *m*-NH_2



22. R = CH_3
23. R = Cl

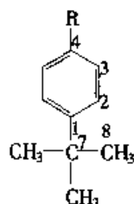


24. R^1 = Br, R^2 = OCH_3
25. R^1 = OH, R^2 = NO_2

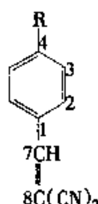
表 12-29 双取代苯 26～33 的^{13}C-NMR 化学位移数据[119,120]①

C \ 化合物	26	27	28	29	30	31	32	33
1	149.6	143.3	129.1	130.7	123.8	134.0	133.0	131.4
2	126.8	126.2	130.1	132.7	133.9	128.5	129.3	130.0
3	128.3	113.5	130.7	132.1	116.6	137.4	137.3	136.9
4	131.3	157.5	146.0	118.2	163.6	116.2	117.3	118.2
7	34.5	34.0	80.9	83.2	77.0			
8	31.3	31.6	160.3	159.4	159.8			
CN			119.2	128.5	127.7			
R		55.0	25.9					

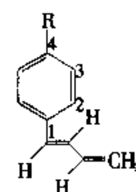
① 化合物 31～33 在 CCl_4 中测定。



26. R = Cl
27. R = OCH_3



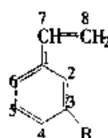
28. R = CH_3
29. R = Br
30. R = OH



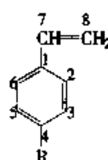
31. R = H
32. R = CH_3
33. R = Cl

表 12-30 双取代苯 34～39 的^{13}C-NMR 化学位移数据[121]

C \ 化合物	34	35	36	37	38	39	C \ 化合物	34	35	36	37	38	39
1	137.4	138.7	137.6	137.7	137.5	144.8	6	123.7	124.6	134.9			
2	128.4	126.8	121.8	128.9	129.0	127.2	7	137.3	134.6	134.9	137.5	136.7	135.9
3	137.4	134.6	148.4	128.9	129.0	124.3	8	112.6	115.0	116.6	114.0	114.8	119.0
4	128.4	126.8	121.8	137.7	134.4	147.7	R	21.2			21.3		
5	128.4	129.2	129.6										



34. R = CH_3
35. R = Cl
36. R = NO_2

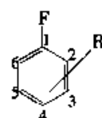


37. R = CH_3
38. R = Cl
39. R = NO_2

表 12-31　双取代苯 40～48 的^{13}C-NMR 化学位移数据[122]①

C \ 化合物	40	41	42	43	44	45	46	47	48
1	148.9	160.1	157.4	163.2	162.6	165.6	150.5	162.3	154.2
2	144.8	100.6	115.8	120.5	114.6	116.0	136.3	99.2	114.5
3	119.9	159.8	114.9	132.4	138.2	132.1	115.8	149.5	114.2
4	113.0	109.6	156.0	126.4	125.5	132.3	123.9	109.3	144.8
5	123.8	130.0		135.1	131.0		115.8	129.3	114.2
6	113.6	106.4		112.0	120.9		114.8	100.9	114.5

① 化合物 43～48 在 $(CD_3)_2SO$ 中测定。



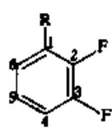
40. R = o-OCH_3　**41.** R = m-OCH_3　**42.** R = p-OCH_3

43. R = o-CHO　**44.** R = m-CHO　**45.** R = p-CHO

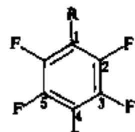
46. R = o-NH_2　**47.** R = m-NH_2　**48.** R = p-NH_2

表 12-32　多取代苯 49～57 的^{13}C-NMR 化学位移数据[125～127]

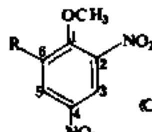
C \ 化合物	49	50	51	52	53	54	55	56	57
1	118.5	140.1	138.6	138.34	100.00	110.88	153.1	155.8	158.5
2	152.2	146.4	141.7		146.53	145.41	145.6	145.4	139.5
3	152.2	152.9	152.4		137.68	137.53	125.3	120.3	122.6
4	118.5	124.3	107.3		141.89	139.58	142.5	143.4	141.7
5	125.9	125.8	125.5				125.3	130.2	130.4
6	125.9	122.4	113.8				145.6	132.6	115.2
CH_3						4.61			
OCH_3							66.4	64.2	58.7



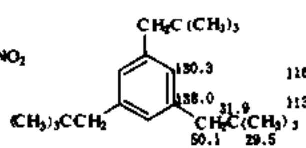
49. R = H　**50.** R = NO_2　**51.** R = NH_2



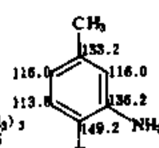
52. R = F　**53.** R = H　**54.** R = CH_3



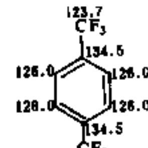
55. R = NO_2　**56.** R = Cl　**57.** R = H



58[123]



59[122]



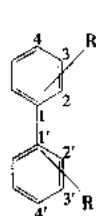
60[124]

四、联苯类化合物的^{13}C-NMR 化学位移

表 12-33　联苯类化合物 61～71 的^{13}C-NMR 化学位移数据[128～132]①

C \ 化合物	61	62	63	64	65	66	67	68	69	70	71
1	141.8	141.9	141.7	138.7	140.0	140.5	141.1				134.4
2	127.8	135.9	128.3	127.1	128.9	129.6	129.2	127.83	128.41	127.24	134.3
3	129.0	130.4	138.3	129.8	129.4	132.6	138.3	128.90	129.10	129.66	127.4
4	127.8	129.9	129.1	136.7	134.1	122.0	93.2				129.8
5		126.4	129.1								
6		127.8	124.7								
1′					140.2	140.9	140.4				
2′					127.3	128.4	127.1	127.46	127.34	127.03	
3′					129.4	129.5	129.2	130.36	130.48	130.28	
4′					127.6	127.5	128.0				
CH_3		20.3	21.9	21.1						21.10	

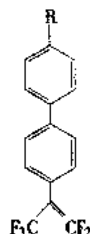
① 化合物 62～67 在四氢呋喃中测定。



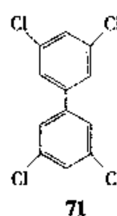
61. R = H
62. R = 2,2′ - CH_3
63. R = 3,3′ - CH_3
64. R = 4,4′ - CH_3



65. R = Cl
66. R = Br
67. R = I

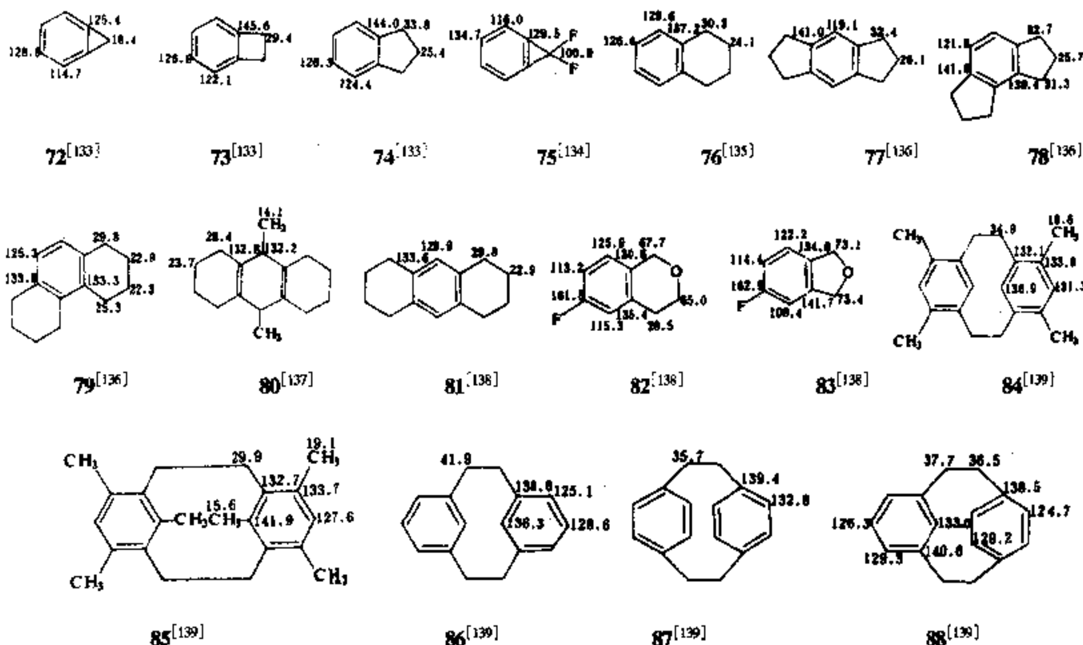


68. R = H
69. R = Cl
70. R = CH_3



71

五、脂环并苯类化合物的^{13}C-NMR 化学位移



六、萘及其衍生物的^{13}C-NMR 化学位移

表 12-34　萘及其衍生物 89 ~ 102 的^{13}C-NMR 化学位移数据[62,108,109,140~146]

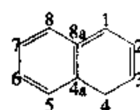
C \ 化合物	89	90	91	92	93	94	95	96	97①	98	99	100	101①	102
1	134.2	126.7	145.9	122.9	151.23	109.61	155.5	118.7	117.73	159.5	117.4	110.4	131.85	
2	126.6	134.7	123.1	148.4	108.79	153.35	103.8	156.6	127.31	109.8	161.7	128.9	136.59	123.64
3	125.8	127.7	125.0	124.7	125.84	117.78	126.4	105.7	109.23	126.0	112.2	125.3	125.30	123.78
4	124.2	127.4	127.4	127.6	120.79	129.91	120.2	129.3	144.73	124.2	131.6	133.6	135.13	134.31
4a	133.9	131.6	135.8	132.3	134.78	129.07	134.5	129.0	124.28	135.7	126.4	132.5	134.08	134.01
5	128.7	127.4	129.6	128.0	127.71	127.82	127.4	127.6	122.37	126.6	129.2	129.1	128.74	128.34
6	125.6	124.8	124.5	125.2	126.45	123.70	125.9	123.5	124.80	127.3	128.7	125.3	125.97	127.00
7	125.6	125.2	124.5	125.7	125.31	126.58	125.1	126.3	126.23	128.1	128.4	127.9	129.03	129.08
8	126.7	126.9	126.8	127.4	121.49	126.43	122.0	126.7	128.87	120.9	128.1	132.9	125.19	122.69
8a	132.9	133.2	132.0	134.0	124.40	134.60	127.5	134.6	135.43	124.3	135.5	133.2	130.69	124.76
CH_3		21.4												

① 化合物 97 在 $(CD_3)_2CO$ 中测定，101 在 CS_2-$(CD_3)_2CO$ 中测定。

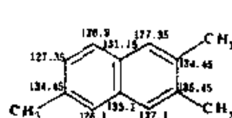
表 12-35 萘及其衍生物 103~111 的^{13}C-NMR 化学位移数据[145,147~150]

C \ 化合物	103	104①	105	106	107	108	109	110	111
1	132.1	134.4	126.7	122.8	120.7	113.4	124.6	146.9	127.3
2	126.0	128.8	134.2	129.7	129.4	129.9	145.4	122.1	135.2
3		124.3	127.7	125.7	126.7	104.3	119.5	124.2	
4		127.5	127.6	127.7	134.1	155.4	128.9	134.2	
4a	132.5	135.2	133.4	134.6	133.7	127.2	136.5	135.1	132.3
5	124.4		126.7	128.1	124.3	122.9	127.3	127.7	126.7
6	125.1		136.2	126.4	126.1	126.0	140.7	137.6	124.8
7			128.6	126.9	126.7	128.0	130.5	131.8	
8			128.0	126.9	127.5	127.2	130.0	122.1	
8a		132.8	131.4	132.0	131.8	133.0	130.5	123.6	
CH_3	19.3	25.6	21.6						20.1
CH_2			34.0						

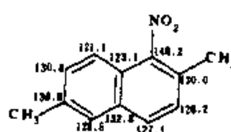
① 化合物 104 在 CCl_4 中测定。



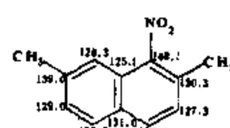
89. 1-CH_3，　**90.** 2-CH_3　**91.** 1-C $(CH_3)_3$
92. 2-C $(CH_3)_3$　**93.** 1-OH　**94.** 2-OH
95. 1-OCH_3　**96.** 2-OCH_3　**97.** 1-NH_2
98. 1-F　**99.** 2-F　**100.** 1-CN
101. 1-CHO　**102.** 1-NO_2　**103.** 1-CH_3，4-CH_3
104. 1-CH_3，8-CH_3　**105.** 2-CH_2Br，6-CH_3　**106.** 1-Br，4-H
107. 1-Br，4-CH_3　**108.** 1-Br，4-OCH_3　**109.** 1-NO_2，6-CH_3
110. 2-NO_2，6-CH_3　**111.** 2-CH_3，3-CH_3



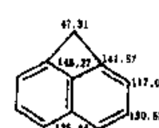
112[151]



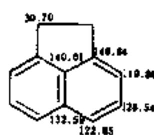
113[150]



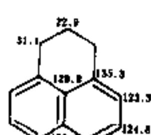
114[150]



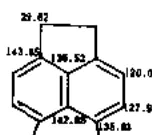
115[152]



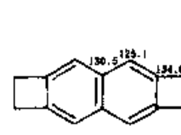
116[109] [$(CD_3)_2CO$]



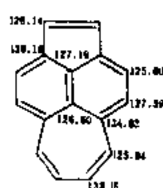
117[148] [CCl_4]



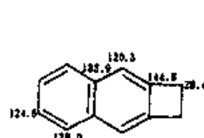
118[153]



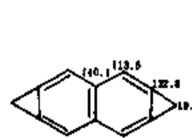
119



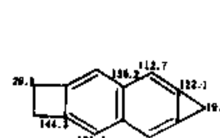
120[153]



121

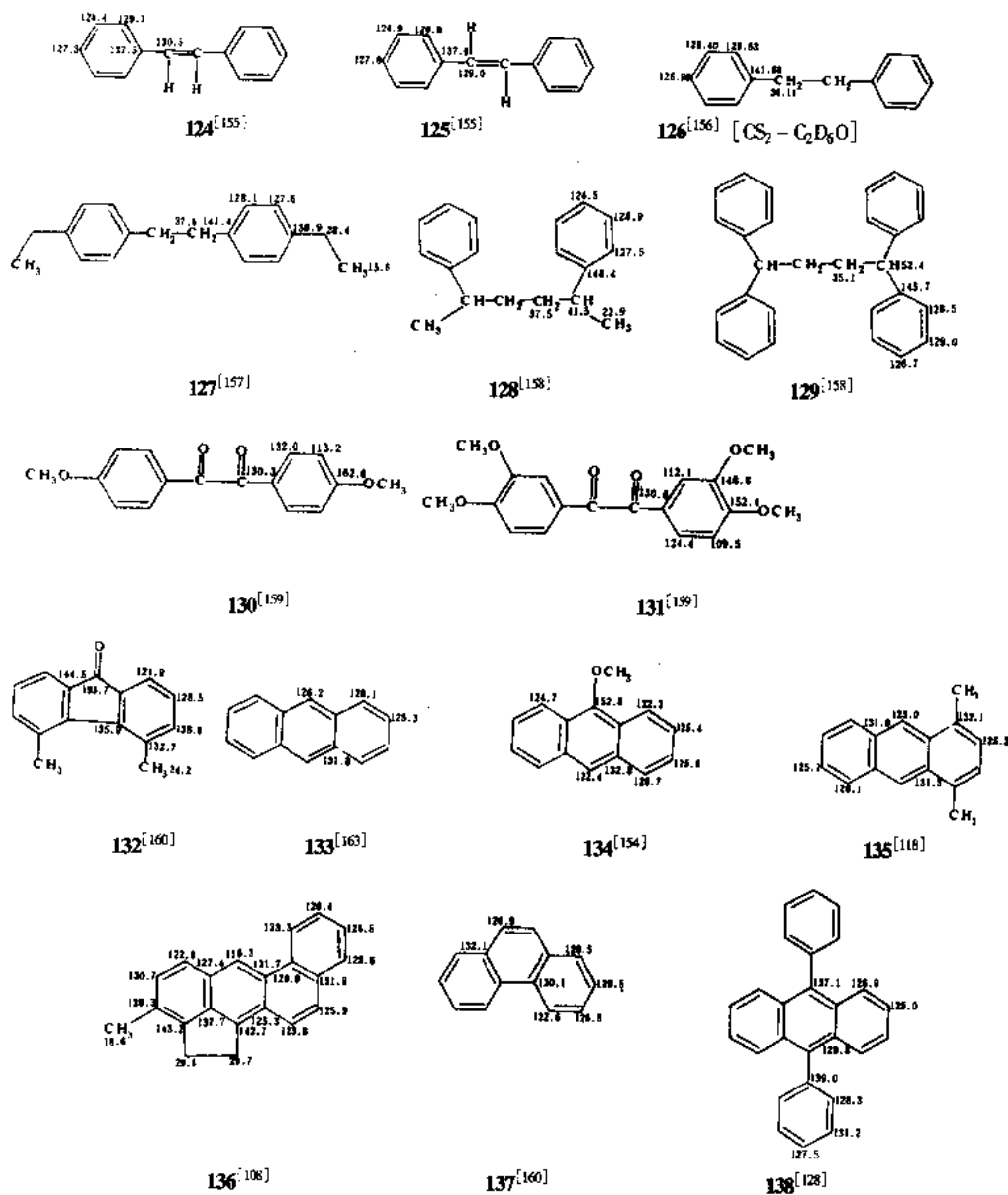


122



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七、其他芳香化合物的^{13}C-NMR 化学位移



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157 Takemura T. Can J Chem, 1976; 54: 3412
158 Takahashi K et al. Org Magn Reson, 1974; 6: 62
159 Vajda M et al. Org Magn Reson, 1976; 8: 324
160 Stothers J B et al. Org Magn Reson, 1977; 9: 408

第十三章　醇、酚及醚类化合物的^{13}C-NMR化学位移

醇、酚和醚类化合物的^{13}C-NMR化学位移的特征：

① 醇类化合物各碳的化学位移与相应的烷烃化学位移进行比较发现羟基使 α 碳向低场位移大约35～52个 δ 单位，β 碳向低场位移5～12个 δ 单位，γ 碳向高场位移大约6个 δ 单位，离羟基更远的碳受羟基的影响小于1个 δ 单位。

② 在脂环醇中，由于立体效应使 γ 碳向高场位移，当羟基为a键构型时尤其明显。

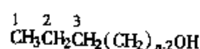
③ 由醇到相应的醚，伯醇和仲醇的 α 碳向低场位移8～11个 δ 单位，而叔醇成醚后，化学位移由于拐折构象（staggered conformation）的 γ-效应，向低场移动较小。

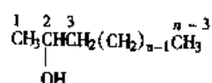
第一节　醇类化合物的^{13}C-NMR化学位移

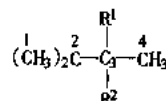
一、饱和醇类化合物的^{13}C-NMR化学位移

表 13-1　开链脂肪醇1～13的^{13}C-NMR化学位移数据[1]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13
1	50.2	58.2	64.8	62.6	63.0	63.1	26.3	23.8	24.5	24.5	20.9	27.5	26.6
2		18.8	27.0	36.2	33.7	34.0	64.6	69.9	68.4	68.4	73.2	73.4	75.3
3			11.2	20.3	29.4	27.0	26.3	33.2	42.4	40.4	36.3	40.0	38.7
4				14.8	23.8	33.2		11.1	20.3	29.5	19.3	18.7	26.8
5					15.0	24.0			15.2	24.1			
6						15.4				15.1			







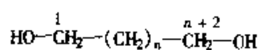
1. $n=0$　**4.** $n=3$　**7.** $n=0$　**9.** $n=2$　**11.** $R^1=R^2=H$

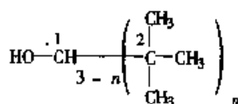
2. $n=1$　**5.** $n=4$　**8.** $n=1$　**10.** $n=3$　**12.** $R^1=CH_3$，$R^2=H$

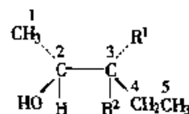
3. $n=2$　**6.** $n=5$　**13.** $R^1=R^2=CH_3$

表 13-2　脂肪醇14～22的^{13}C-NMR化学位移数据[2~4]

C \ 化合物	14	15	16	17	18	19	20	21	22
1	64.6	60.2	63.0	63.1	73.29	85.62	84.94	19.24	20.22
2		36.4	30.3	33.7	32.66	37.37	44.80	70.68	70.36
3				23.5	26.20	28.78	32.37	41.84	41.84
4								25.61	25.55
5								11.86	12.06
R								14.12	14.02



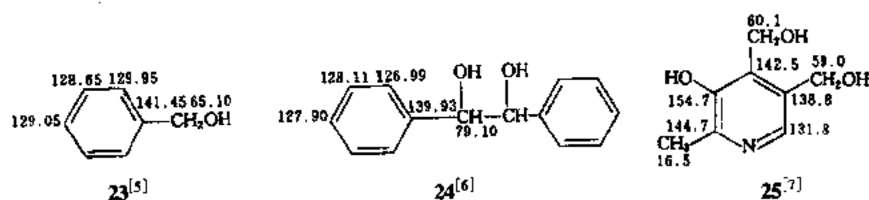




14. $n=0$　**16.** $n=2$　**18.** $n=1$　**21.** $R^1=CH_3$，$R^2=H$

15. $n=1$　**17.** $n=3$　**19.** $n=2$　**22.** $R^1=H$，$R^2=CH_3$

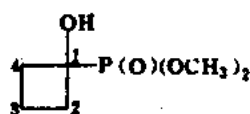
20. $n=3$



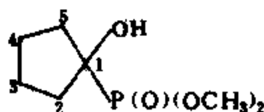
23[5]　　24[6]　　25[7]

表 13-3　环醇化合物 26～36 的 ^{13}C-NMR 化学位移数据[8～11]

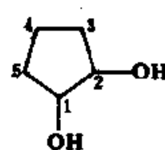
C \ 化合物	26	27	28	29	30	31	32	33	34	35	36
1	71.9	79.0	74.8	79.7	73.4	73.2	66.7	68.1	80.8	49.0	43.4
2	33.0	36.7	74.8	79.7	44.6	44.9	42.5	41.0	41.6	72.6	41.2
3	13.4	24.1	31.2	32.4	73.4	72.2	29.6	30.3	30.9	38.8	76.1
4			20.3	21.3	34.0	33.7	25.9	26.5	13.8	20.3	
5			31.2	32.4	34.0	33.7		27.3			
OCH_3	53.7	53.5							53.8		



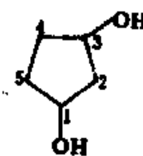
26



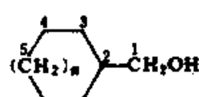
27



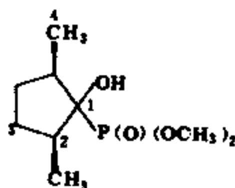
28. 顺式
29. 反式



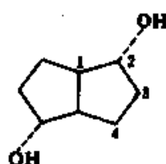
30. 顺式
31. 反式



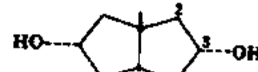
32. $n=0$
33. $n=1$



34



35



36

表 13-4　环醇化合物 37～42 的 ^{13}C-NMR 化学位移数据[12～14]

C \ 化合物	37①	38①	39	40	41	42
1	64.9	69.7	66.7	72.2	70.9	68.9
2	32.6	35.6	35.0	37.5	33.7	31.1
3	20.6	25.5	22.6	27.5	33.7	31.1
4		26.1	49.8	49.0	70.9	68.9
5			34.0	33.7		
6			29.4	29.4		

① 化合物 37，38 在 CS_2 中测定。

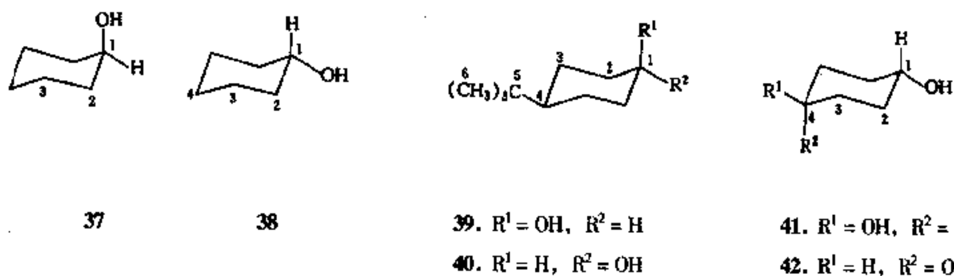
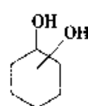


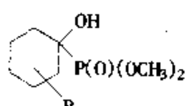
表 13-5 环醇化合物 43 ~ 54 的 ^{13}C-NMR 化学位移数据[8,13,15]①

C \ 化合物	43	44	45	46	47	48	49	50	51	52	53	54
1	72.3	76.6	70.3	68.2	68.9	70.9	71.6	74.6	72.0	71.9	74.8	69.8
2	72.3	76.6	45.8	43.1	31.1	33.7	31.7	36.2	39.8	30.6	79.2	74.1
3	32.1	34.5	70.3	68.2	31.1	33.7	20.1	29.9	26.0	28.7	50.2	42.4
4	23.0	26.0	36.0	35.1	68.9	70.9	25.4	25.8	34.3	28.1	32.9	24.1
5	23.0	26.0	22.4	20.8	31.1	33.7	20.1	20.0	20.0	28.7	23.7	19.8
6	32.1	34.5	36.0	35.1	31.1	33.7	31.7	33.4	31.0	30.6	33.1	27.5
7							53.5	53.4	53.0	53.3		
R								17.2	22.5	19.4		

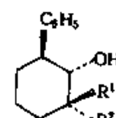
① 化合物 43 ~ 48 在 H_2O 中测定。



43. 1, 2-*cis*
44. 1, 2-*trans*
45. 1, 3-*cis*
46. 1, 3-*trans*
47. 4, 1-*cis*
48. 4, 1-*trans*



49. R = H
50. 2-*trans*-CH_3
51. 3-*cis*-CH_3
52. 4-*trans*-CH_3



53. R^1 = H, R^2 = OH
54. R^1 = OH, R^2 = H

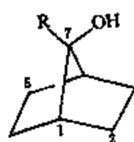
表 13-6 环醇化合物 55 ~ 59 的 ^{13}C-NMR 化学位移数据[16,17]

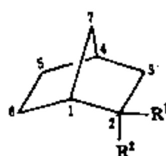
C \ 化合物	55	56	57	58	59	C \ 化合物	55	56	57	58	59
1				41.2	43.7	8	12.24	13.22	11.43	21.7	21.0

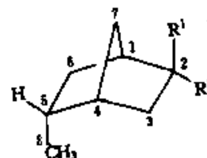
表 13-7　环醇化合物 60～72 的^{13}C-NMR 化学位移数据[18～21]

C \ 化合物	60	61	62	63	64	65	66	67	68	69	70	71①	72①
1	40.4	44.3	41.8	42.5	44.2	45.5	43.7	49.1	48.5	46.3	44.1	49.7	49.0
2	27.1	28.3	28.2	72.9	74.7	74.6	73.3	77.8	77.1	83.9	80.5	77.0	79.6
3				39.4	42.4	34.8	31.5	48.6	46.8	42.8	38.0	39.2	40.9
4				37.2	35.4	40.7	42.7	37.0	37.4	48.0	48.4	45.6	45.5
5	27.1	29.2	29.4	29.9	28.1	32.4	34.3	28.0	28.4	25.1	24.7	28.6	27.6
6				20.0	24.4	33.3	27.6	24.0	22.2	23.9	18.3	26.3	34.3
7	79.0	84.0	86.3	37.6	34.4	36.2	39.5	37.4	38.7	35.2	33.9	48.3	46.5
8						16.9	16.5			23.2	30.6	18.8	20.4
9			26.2							26.2	20.2	20.3	20.7
R		20.8	9.1					25.8	30.5			13.5	11.5

① 化合物 71、72 在 C_6D_6 中测定。



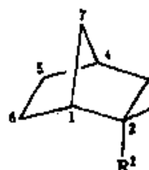


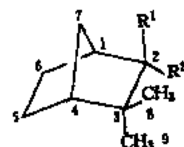


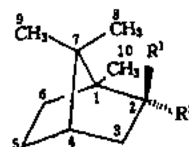
60. R = H　**61.** R = CH_3　**62.** R = CH_2CH_3

63. R^1 = H，R^2 = OH　**64.** R^1 = OH，R^2 = H

65. R^1 = OH，R^2 = H　**66.** R^1 = H，R^2 = OH







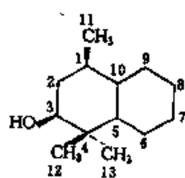
67. R^1 = OH，R^2 = CH_3　**68.** R^1 = CH_3，R^2 = OH

69. R^1 = OH，R^2 = H　**70.** R^1 = H，R^2 = OH

71. R^1 = OH，R^2 = H　**72.** R^1 = H，R^2 = OH

表 13-8　环醇化合物 73～82 的^{13}C-NMR 化学位移数据[22～26]

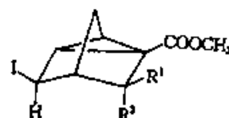
C \ 化合物	73	74	75	76	77	78	79	80	81	82
1	29.84	39.7	46.2	25.2	26.7	13.2	13.0	32.2	41.7	42.7
2	27.35	26.4	72.0	36.8	35.6	15.9	21.5	26.2	71.3	72.5
3	78.57	26.4	39.2	80.8	82.2	77.0	81.6		26.9	28.3
4	38.41	39.7	38.8	49.4	49.1	35.6	40.6	43.7	26.5	30.7
5	52.19	29.1	34.9	26.0	29.1	29.4	31.9		34.3	33.7
6	21.39	39.1	38.2	34.8	32.1	10.7	13.0	48.3	28.4	28.5
7	21.50			33.6	30.0	30.6	31.9	28.0	26.8	23.3
8	27.26								32.1	37.3
9	44.80							73.4		
10	33.82									
11	18.99									
12	27.35									
13	14.89									
OCH_3				51.4	51.3					
				52.6	52.3					
CO				172.9	171.5					
R							22.0			



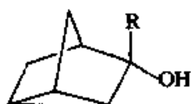
73



74. R = H
75. R = OH



76. R^1 = OH, R^2 = $COOCH_3$
77. R^1 = $COOCH_3$, R^2 = OH



78. R = H
79. R = CH_3



80

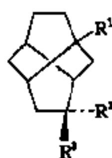


81. R^1 = OH, R^2 = H
82. R^1 = H, R^2 = OH

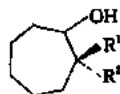
表 13-9 环醇化合物 83~95 的^{13}C-NMR 化学位移数据[27~31]

C \ 化合物	83	84	85	86①	87①	88①	89	90	91	92	93	94	95
1	72.4	26.0	26.7	72.2	77.6	73.5	42.7	41.7	29.0	30.2	71.59	68.11	34.52
2	37.9	27.1	22.0	38.0	42.0	38.7	72.5	71.3	35.7	36.7	34.73	32.29	31.86
3	30.2	35.0	37.4	23.6	32.0	29.7	28.3	26.5	22.4	21.8	23.24	20.94	21.65
4	24.0	71.2	68.8	28.9	26.0	25.8	30.7	26.9		26.6	27.96	24.27	
5	21.9	36.2	35.4		28.1	28.0	33.7	34.3		36.8	25.70	23.38	
6	37.5	28.8	29.1		22.1	22.2	28.5	28.4		70.0		23.30	24.57
7	29.8	29.0	28.4		36.3	34.6	23.3	26.8	25.9	38.3		23.85	21.0
8	28.6	24.6	28.2				37.3	32.1	25.9	24.4			
9	26.6	24.2	24.2							23.7			73.01
10	33.7	25.3	24.6										
R					20.1	17.6							

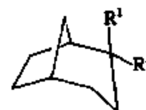
① 化合物 86~88 在 CS_2 中测定。



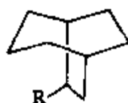
83. R^1 = OH, R^2 = R^3 = H
84. R^1 = R^3 = H, R^2 = OH
85. R^1 = R^2 = H, R^3 = OH



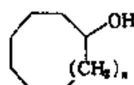
86. R^1 = R^2 = H
87. R^1 = H, R^2 = CH_3
88. R^1 = CH_3, R^2 = H



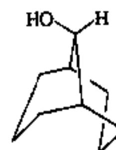
89. R^1 = H, R^2 = OH
90. R^1 = OH, R^2 = H



91. R = H
92. R = OH



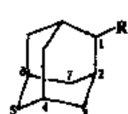
93. n = 1
94. n = 5



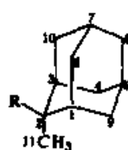
95

表 13-10 环醇化合物 96～103 的^{13}C-NMR 化学位移数据[27,32-35]

C \ 化合物	96	97	98	99	100	101	102	103
1	74.7	83.3	77.0	39.0	42.1	34.0	79.62	83.40
2	34.7	31.5	32.0	73.7	69.7	77.3	48.74	50.03
3	31.2	31.5	31.9	39.0	42.1	34.0	28.20	42.27
4	27.8	27.6	27.4	32.9	34.6	32.2	27.90	144.24
5	37.8	37.7	37.5	27.5	27.5	27.2	27.23	
6	27.3	27.6	27.2	38.3	39.5	32.2	37.04	
7	36.7	36.6	36.5	27.1	27.4	33.8	49.65	
8				34.4	36.0	26.7		
9				34.4	36.0	33.8		
10				32.9	34.6	38.2		
11				34.4	32.8	53.6		126.71
12								129.54
			170.2					
R		55.3	21.4					



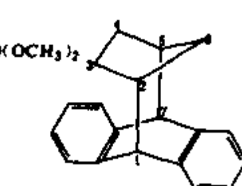
96. R = OH
97. R = OCH_3
98. R = $OCOCH_3$



99. R = OH
100. R = Br



101



102



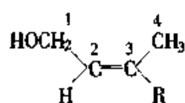
103

二、不饱和醇类化合物的^{13}C-NMR 化学位移

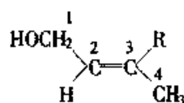
表 13-11 不饱和醇化合物 104～115 的^{13}C-NMR 化学位移数据[36-38]

C \ 化合物①	104	105	106	107	108	109	110	111	112	113	114	115
1	57.9	56.6	62.9	60.1	63.3	58.8	66.3	67.0	58.3	62.22	62.22	61.41
2	131.4	128.3	132.1	127.0	139.1	125.7	36.9	43.7	124.2	32.04	36.13	23.18
3	125.3	132.5	126.0	130.7	113.7	133.7	134.7	134.9	137.4	132.72	133.40	76.43
4	12.7	20.7	17.3	25.6			117.2	118.0	39.4	125.40	126.18	82.25
5									26.4	27.18	32.52	18.50
6									124.2	30.96	31.84	31.21
7									130.9	22.47	22.35	22.03
8									15.6	13.97	13.97	13.60
9									17.1			
10						17.6			25.1			
R						25.4		22.7				

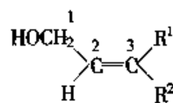
① 化合物 104～109 在二氧六环中测定。



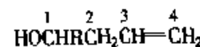
104. R = H
105. R = Cl



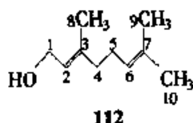
106. R = H
107. R = Cl



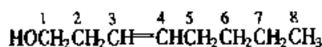
108. $R^1 = R^2 = H$
109. $R^1 = R^2 = CH_3$



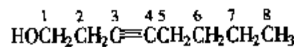
110. R = H
111. $R = CH_3$



112



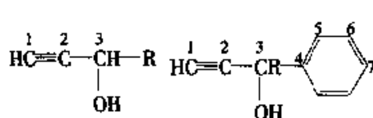
113. *cis*
114. *trans*



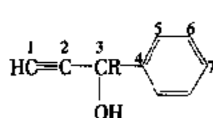
115

表 13-12 不饱和醇化合物 116～128 的 ^{13}C-NMR 化学位移数据[39,40]

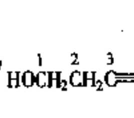
C \ 化合物	116	117	118	119	120	121	122	123	124	125	126	127	128
1	73.8	72.0	72.9	74.9	73.1	60.7	74.6	74.0	50.3	57.8	113.47	114.1	113.4
2	82.0	85.8	84.9	83.6	87.2	22.9	82.8	83.6	83.7	85.6	135.97	139.7	139.07
3	50.4	57.7	63.3	63.6	69.7	80.7	62.6	62.6			53.94	58.40	57.90
4				139.9	144.9	70.5	136.6	129.9			72.85	77	76.49
5				126.6	124.9		116.7	128.6			51.73	52.6	54.91
6				128.3	128.2								
7				128.3	127.6								
			30.6										
R		24.0	9.4		33.1			17.4		24.1			



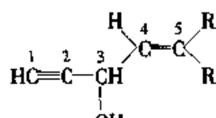
116. R = H
117. $R = CH_3$
118. $R = CH_2CH_3$



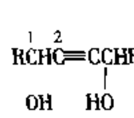
119. R = H
120. $R = CH_3$



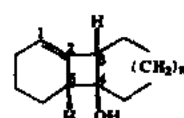
121



122. R = H
123. $R = CH_3$



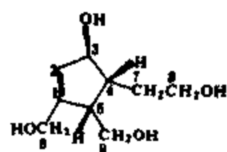
124. R = H
125. $R = CH_3$



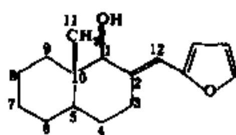
126. *n* = 2
127. *n* = 3
128. *n* = 4

表 13-13 不饱和醇化合物 129～141 的 ^{13}C-NMR 化学位移数据[19,20,23,41～44]

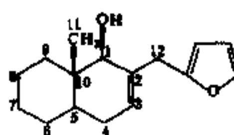
C \ 化合物	129	130	131	132	133	134	135	136	137	138	139	140	141
1	147.26	81.6	79.2	45.6	47.4	54.2	53.8	50.1	48.2	48.2	48.3	155.1	144.6
2	130.77	141.2	136.2	134.3	131.9	78.6	78.2	72.3	72.3	145.3	145.6	96.1	116.3
3	81.84	29.2	124.8			43.1	49.3	36.9	37.6	127.6	124.6	21.3	131.9
4	48.55	27.9	30.3			42.0	42.9	40.7	42.9	40.3	41.0	19.3	131.9
5	48.74	44.2	39.6	21.4	22.2	138.1	139.1	140.2	140.0	73.3	74.6		115.7
6	62.02	28.4	28.4			134.3	133.8	133.5	131.1	32.2	35.7		144.0
7	31.07	26.4	26.3	82.0	86.9	48.2	44.5	45.6	48.2	34.5	34.3		98.8
8	60.17	21.7	21.9							41.2	47.9		65.3
9	60.36	37.3	37.6							21.8	21.6		40.0
10		41.3	37.6							21.9	21.9		
11		10.2	10.3							28.3	29.3		
12		108.3	32.2							31.5	30.9		
R						27.5	28.6						



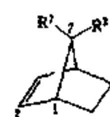
129



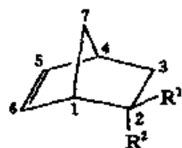
130



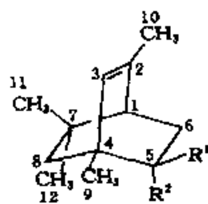
131



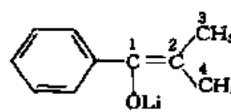
132. $R^1 = H$, $R^2 = OH$
133. $R^1 = OH$, $R^2 = H$



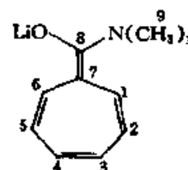
134. $R^1 = OH$, $R^2 = CH_3$
135. $R^1 = CH_3$, $R^2 = OH$
136. $R^1 = OH$, $R^2 = H$
137. $R^1 = H$, $R^2 = OH$



138. $R^1 = H$, $R^2 = OH$
139. $R^1 = OH$, $R^2 = H$



140



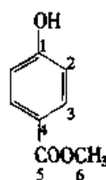
141

第二节　酚类化合物的^{13}C-NMR化学位移

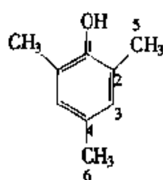
表 13-14　酚类化合物 1～8 的^{13}C-NMR化学位移数据[45,46]

C \ 化合物	1	2	3	4	5	6	7①	8
1	162.5	150.1	157.8	152.6	149.9	153.8	155.72	155.62
2	115.8	123.1	137.4	137.3	133.7	135.8	116.80	115.88
3	132.2	129.3	129.5	110.6	123.4	124.8	131.14	129.58
4	122.3	129.5	103.3	147.8	120.6	119.6	128.65	130.21
5	167.0	15.9	34.6	34.6			30.19	32.58
6	51.6	20.4	30.0	30.3			59.49	61.55
7							43.80	44.87
R			120.2	55.5				

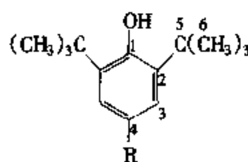
① 化合物 7 在水中测定。



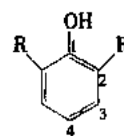
1



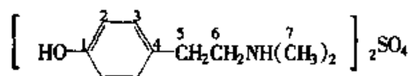
2



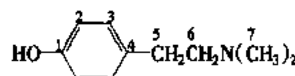
3. R = CN
4. R = OCH_3



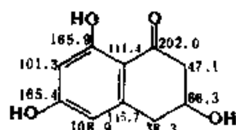
5. R = $CH(CH_3)_2$
6. R = $C(CH_3)_3$



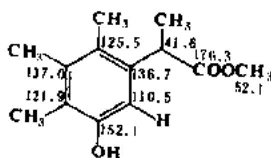
7



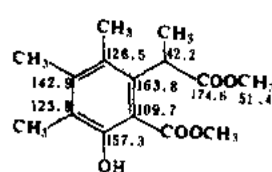
8



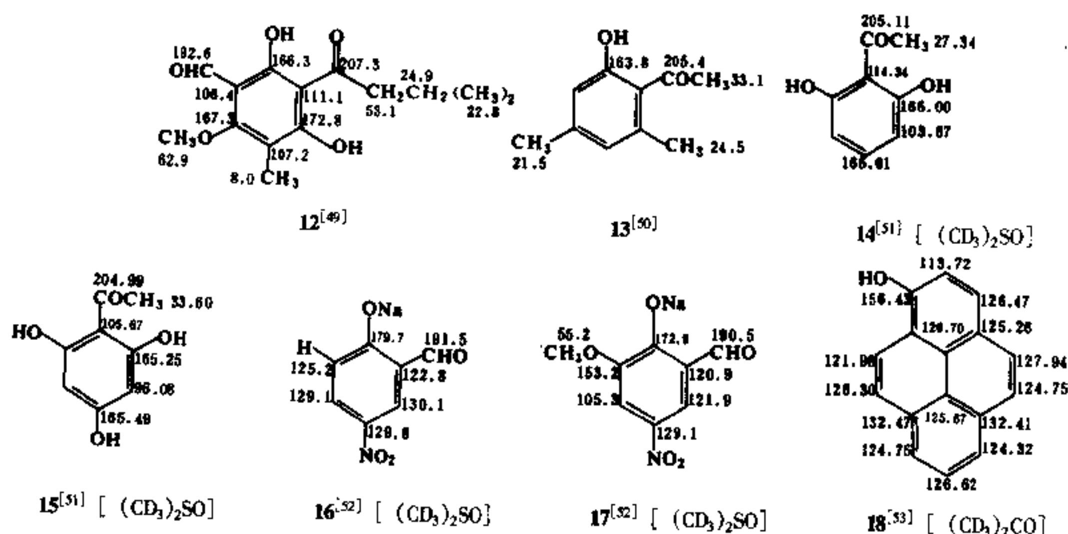
9[47]



10[48]



11[48]



第三节 醚类化合物的^{13}C-NMR 化学位移

一、脂肪醚类化合物的^{13}C-NMR 化学位移

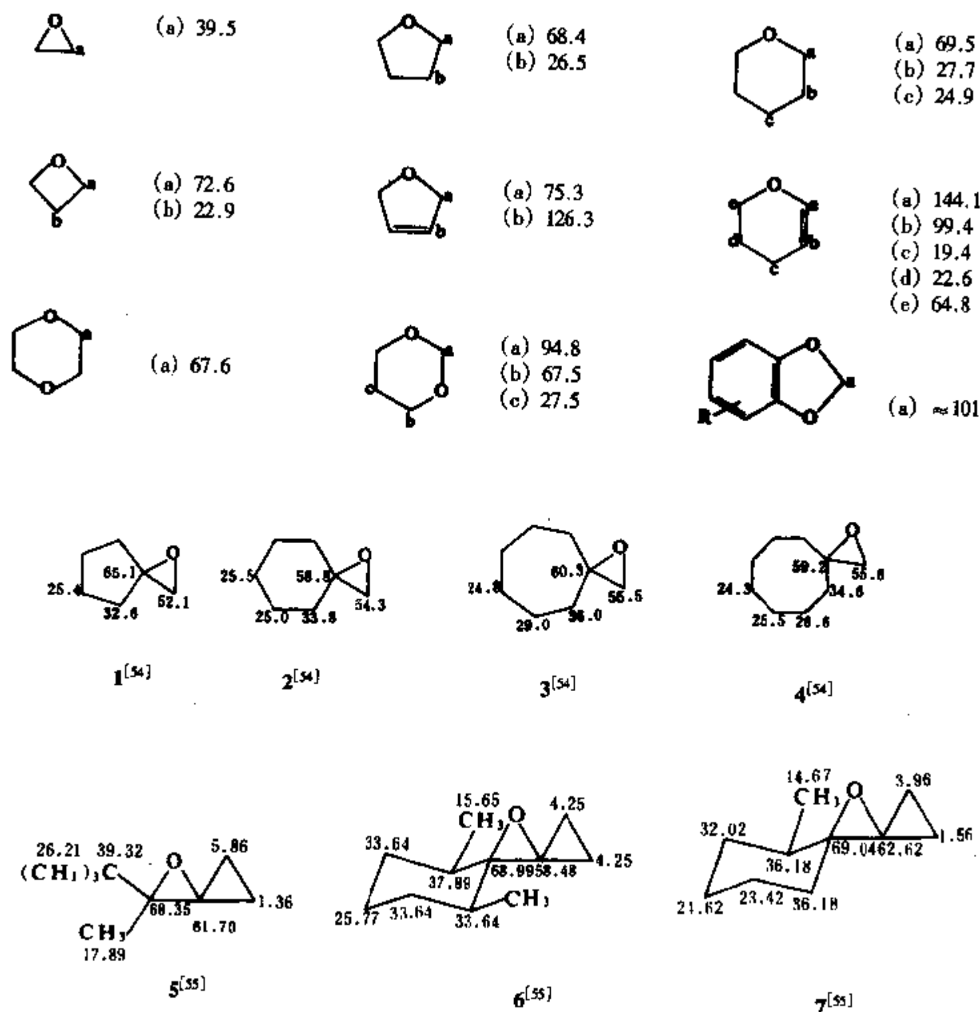
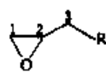
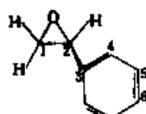
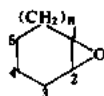


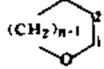
表 13-15　环醚化合物 8～19 的^{13}C-NMR 化学位移数据[56,57]

C \ 化合物	8	9	10	11	12	13	14	15	16	17	18	19
1	47.7	47.0	48.7	51.0	52.2	55.9	39.7	72.8	68.6	69.7	41.73	47.32
2	48.1	51.6	52.0	52.4				23.1	26.7	27.9	54.84	55.68
3	18.0	45.5	33.0	138.5	24.7	26.8				25.1		
4				126.0	19.6	26.6						
5				129.0		25.8						
6				128.7								

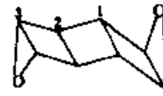












8. R = H
9. R = Cl
10. R = CH_3

11

12. $n=1$
13. $n=3$

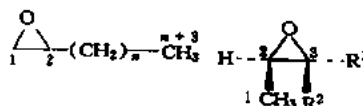
14. $n=0$
15. $n=1$
16. $n=2$
17. $n=3$

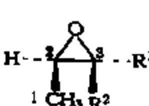
18

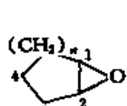
19

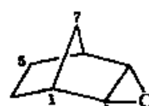
表 13-16　三元环醚化合物 20～32 的^{13}C-NMR 化学位移数据[54]

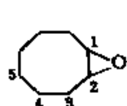
C \ 化合物	20	21	22	23	24	25	26	27	28	29	30	31	32
1	47.8	46.8	46.8	12.9	17.6	14.2	57.0	51.9	55.9	37.7	36.8	55.6	59.5
2	48.0	52.0	52.2	52.4	55.2	59.9				62.0	51.0		
3	18.1	34.9	32.5			58.1	27.3	24.7	29.2			26.7	32.7
4		19.6	28.4				18.4	19.7	24.6			26.5	28.6
5		14.0	22.8						31.2	25.5	25.3	25.8	28.6
6			14.1										
7										50.4	26.3		
R^1						18.5							
R^2						24.8							

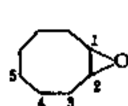












20. $n=0$
21. $n=2$
22. $n=3$

23. $R^1=CH_3$，$R^2=H$
24. $R^1=H$，$R^2=CH_3$
25. $R^1=R^2=CH_3$

26. $n=1$
27. $n=2$
28. $n=3$

29. 氧桥向外
30. 氧桥向内

31

32

表 13-17　环醚化合物 33～42 的^{13}C-NMR 化学位移数据[6,30,58,59]

C \ 化合物	33①	34	35	36	37	38	39	40	41	42
1	134.9	149.3	147.3	83.19	81.14	78.76		77.7	78.2	77.4
2	121.0	81.6	80.8	32.44	31.33	28.64	58.79	36.2	34.5	34.7
3	75.5	35.2	33.3	24.08	23.32	20.90	137.18	24.4	24.7	24.6
4	41.1	25.1	20.4		28.04	25.43	125.52		24	24.1
5	30.9	27.9	27.6		25.91	23.54	128.55		33.2	27.9
6	44.4	34.9	30.3			23.54	128.30		85.1	79.2
7	23.7	104.2	111.8			25.00		31.6	79.6	73.2
8	26.5								39.5	37
9	31.2									
OCH_3	55.5	57.1	55.2	56.03	55.60	55.76				

① 化合物 33 在 CF_2Br_2-CD_2Cl_2 中测定。

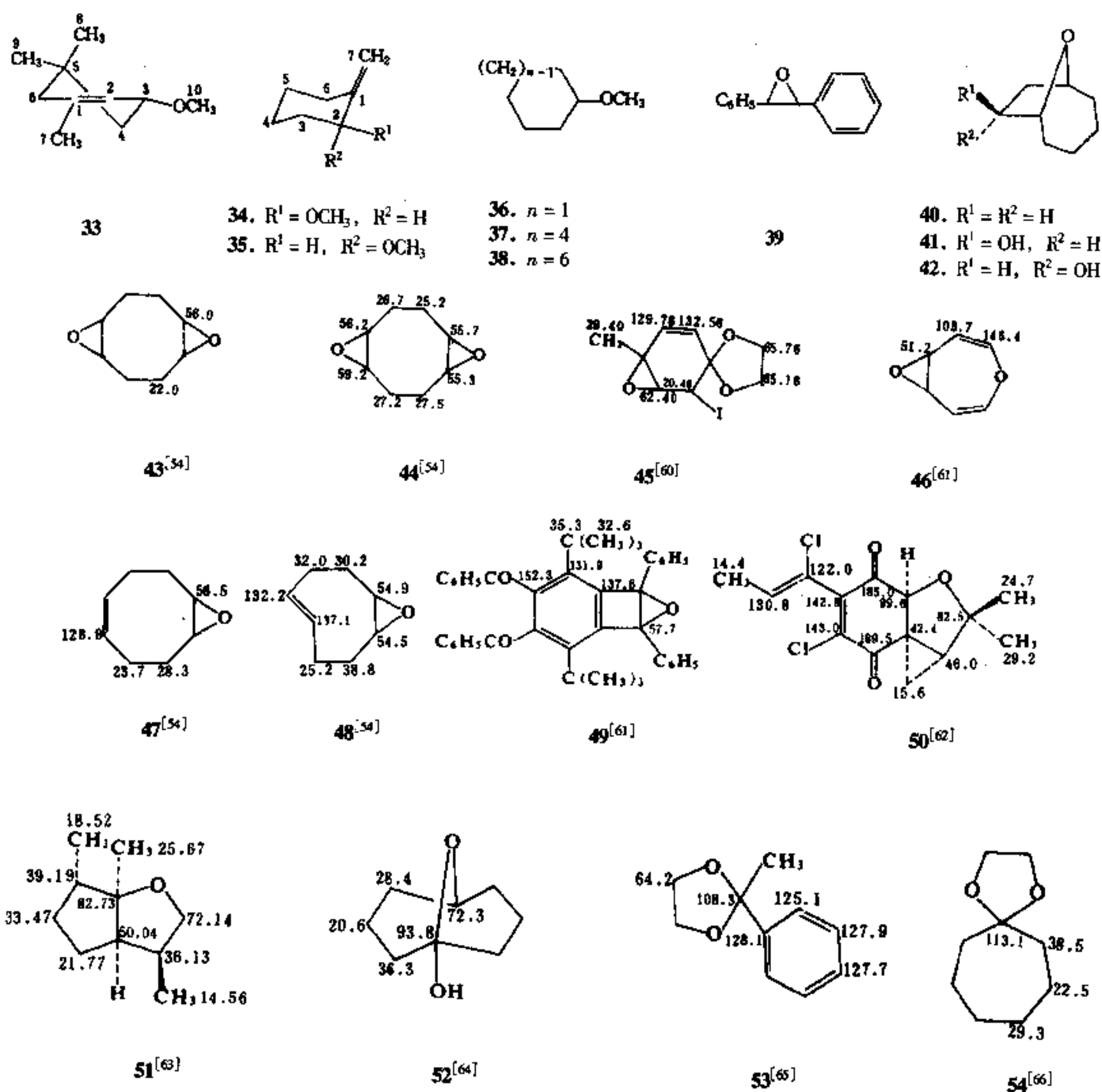
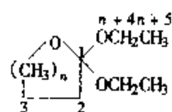


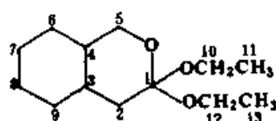
表 13-18 环醚化合物 55 ~ 66 的 ^{13}C-NMR 化学位移数据[67~69]

C \ 化合物①	55	56	57	58	59	60	61	62	63	64	65	66
1	118.4	111.8	112.4	58.5	55.7	56.8	53.2	52.2	51.4	66.5	33.2	52.3
2	30.9	31.6	38.4	84.4	84.4	86.9	49.1	47.5	47.6	29.3	32.1	26.4
3	28.1	20.8	37.4				46.8	44.9	46.8	18.8	21.6	20.4
4	63.6	25.1	41.2	81.8	81.7	93.6	24.0	22.9	22.4			
5	57.0	64.1	68.7	33.0	31.7	34.4	36.4	37.3	36.7			
6	15.2	56.3	32.8	28.6	28.7	26.8	83.5	84.8	84.6			
7		15.3	26.0	37.8	37.9	44.1						
8			26.0	43.8	43.9	47.8	79.8	88.0	88.4			
9			27.4	51.3	51.4	51.4	37.7	76.8	64.5			
10			57.2	32.0	30.7	134.0	38.8	45.6	46.5			
11			15.3	72.5	75.1	128.3	41.3	37.2	38.1			
12			55.2									
13			15.3									
R					21.0							

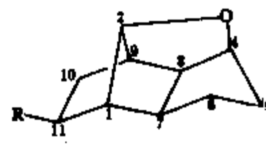
① 化合物 61 ~ 63 在丙酮中测定。



55. $n=1$
56. $n=2$



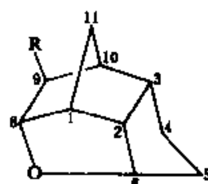
57



58. R = OH
59. R = $OCOCH_3$



60



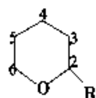
61. R = H
62. R = OH
63. R = Cl

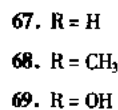


64. X = O
65. X = S
66. X = NCH_3

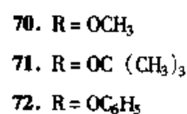
表 13-19 环醚化合物 67～82 的^{13}C-NMR 化学位移数据[70～72]

C \ 化合物	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82
1												79.07	80.20			
2	68.8	74.0	94.2	99.9	94.1	96.5	94.1	81.4	92.6	96.9	101.0	33.09	28.54	95.1	101.7	95.0
3	27.4	34.4	32.6	31.2	30.8	30.8	30.4	31.9	29.6	39.5	40.8	32.59	33.65			
4	24.3	24.3	20.7	19.8	19.6	19.3	24.4	21.9	19.2	24.8	30.0	33.58	35.94	64.7	65.0	72.3
5		26.6	26.1	26.3	25.8	25.7	26.7	26.4	25.6	35.0	34.6	111.59	110.71	64.7	65.0	71.0
6		68.4	63.3	61.6	62.4	61.9	67.4	63.6	63.2	59.6	65.2					
7												70.06	64.50			
10												16.36	16.37			
11												27.35	27.44			
12												7.01	7.02			
R		22.5								22.6	22.2	17.92	16.89		19.8	18.1

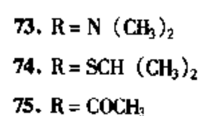




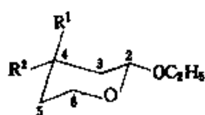
67. R = H
68. R = CH_3
69. R = OH



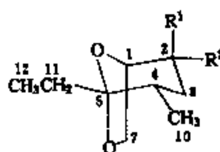
70. R = OCH_3
71. R = OC $(CH_3)_3$
72. R = OC_6H_5



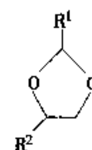
73. R = N $(CH_3)_2$
74. R = SCH $(CH_3)_2$
75. R = $COCH_3$



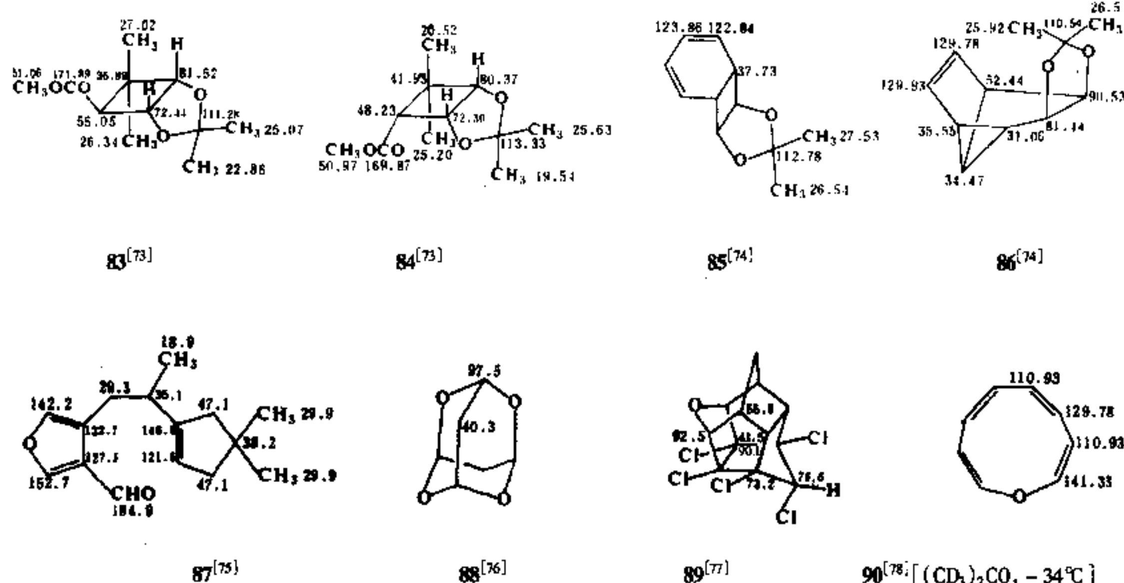
76. $R^1 = CH_3$, $R^2 = H$
77. $R^1 = H$, $R^2 = CH_3$



78. $R^1 = CH_3$, $R^2 = H$
79. $R^1 = H$, $R^2 = CH_3$



80. $R^1 = R^2 = H$
81. $R^1 = CH_3$, $R^2 = H$
82. $R^1 = H$, $R^2 = CH_3$

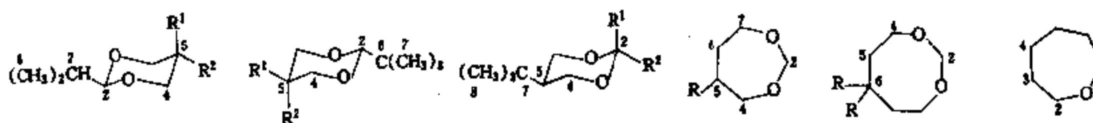


83[73]　84[73]　85[74]　86[74]

87[75]　88[76]　89[77]　90[78] [$(CD_3)_2CO$, -34℃]

表 13-20　环醚化合物 91～102 的 ^{13}C-NMR 化学位移数据[78～83]

C \ 化合物	91	92	93	94	95	96	97	98	99	100	101	102
2	105.98	105.83	108.11	107.72	93.65	99.07	99.37	94.67	94.65	95.7	95.1	70.1
3												31.0
4	67.32	69.27	71.98	73.61	68.53	68.58	67.31	67.24	72.40	69.0	65.7	27.0
5	36.71	37.11	29.72	29.71	44.39	44.62	43.61	30.05	34.95	30.4	42.7	
6			35.31	35.27					38.44	23.2	32.9	
7	32.72	32.56	27.70	24.87	30.66	30.54	32.63		64.84			
8	16.77	17.07			27.58	27.68	29.71					
R	61.35	60.66	15.93	12.40		21.24	21.35		17.27		29.3	



91. $R^1 = CH_2OH, R^2 = H$　**93.** $R^1 = H, R^2 = CH_3$　**95.** $R^1 = R^2 = H$　**98.** R = H　**100.** R = H　**102**

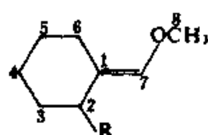
92. $R^1 = H, R^2 = CH_2OH$　**94.** $R^1 = CH_3, R^2 = H$　**96.** $R^1 = H, R^2 = CH_3$,　**99.** $R = CH_3$　**101.** $R = CH_3$

97. $R^1 = CH_3, R^2 = H$

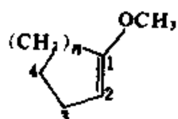
表 13-21　烯醚类化合物 103～113 的 ^{13}C-NMR 化学位移数据[84～87]

C \ 化合物①	103	104	105	106	107	108	109	110	111	112	113
1	118.4	116.6	161.1	155.5	158.3	156.69	150.34	160.98	157.2	159.1	157.9
2	30.6	77.8	92.3	92.0	93.5	117.00	118.45	116.06	117.6	118.5	118.2
3	28.9	33.6	28.6	22.7	24.3	129.23	114.29	125.52	130.3	140.0	135.7
4	27.1	21.4	21.1	23.3	31.0	122.74	155.51	147.95	123.8	124.6	124.0
5	27.1	26.4	31.4	22.7	25.8	147.95	149.30	145.82	130.3	130.0	131.1
6	25.6	21.4		27.2	25.8	94.64	93.06	98.59	117.6	114.7	115.9
7	138.8	141.0			29.5				148.5	148.7	147.7
8	59.1	58.7			28.3				95.9	95.5	97.4
CH_3			55.6	54.0	53.3						
R		54.3								22.4	

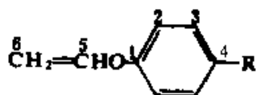
① 化合物 105～107 在 CCl_4 中测定。



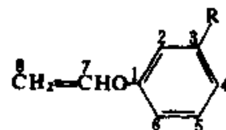
103. R = H
104. R = OCH_3



105. n = 1
106. n = 2
107. n = 3



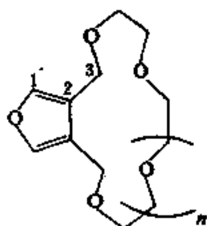
108. R = H
109. R = OCH_3
110. R = NO_2



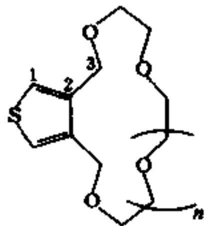
111. R = H
112. R = CH_3
113. R = Cl

表 13-22 环多醚化合物 114～121 的^{13}C-NMR 化学位移数据

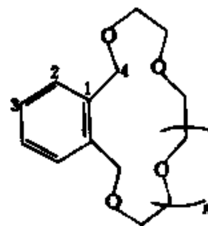
C \ 化合物	114	115	116	117	118	119	120	121
1	141.48	141.29	134.53	134.27	134.27	128.20	137.06	136.87
2	122.51	122.31	134.14	134.01	133.94	130.57	129.01	128.36
3	63.56	63.95	65.12	64.99	64.80	128.29	127.77	127.51
4						71.87	71.62	71.23
OCH_2CH_2O	71.29	71.10	71.75	71.10	70.84	71.72	71.16	70.97
	70.19	70.97	70.19	70.64	69.12	69.99	70.06	70.58
	69.21	70.57	69.28	69.47			69.34	69.73
		69.60						



114. n = 1
115. n = 2



116. n = 1
117. n = 2
118. n = 3

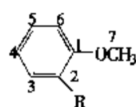


119. n = 0
120. n = 1
121. n = 2

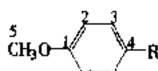
二、芳香醚类化合物的^{13}C-NMR 化学位移

表 13-23 芳香醚类化合物 122～134 的^{13}C-NMR 化学位移数据[89,90]

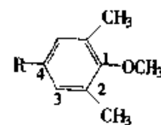
C \ 化合物	122	123	124	125	126	127	128	129	130	131	132	133	134
1	157.6	153.0	159.8	158.4	158.8	164.7	157.1	156.6	162.8	148.1	159.7	154.5	151.7
2	130.5	139.9	114.1	114.2	115.8	114.5	130.2	133.6	133.2	141.8	112.6	131.7	130.1
3	126.5	125.8	129.6	130.4	129.9	130.5	128.5	129.2	125.2	125.3	138.6	126.8	127.3
4	120.3	120.9	120.7	129.6	125.4	130.2	123.5	129.2	144.2	127.1	119.7	121.8	124.5
5	126.5	134.5	54.7	55.2	54.6	56.1					129.6	129.7	131.5
6	110.2	114.3									119.7	119.6	120.7
7	55.3	57.4								164.4		16.0	15.8
8										115.6		157.8	162.4
9										126.3		117.4	115.8
10										142.8		129.3	125.5
11												122.1	141.8
R	16.0												



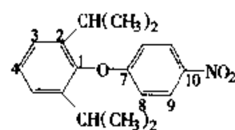
122. R = CH_3
123. R = NO_2



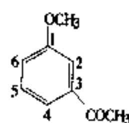
124. R = H
125. R = CH_3
126. R = Cl
127. R = CHO



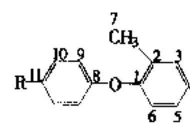
128. R = H
129. R = Cl
130. R = NO_2



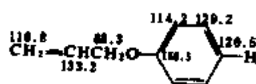
131



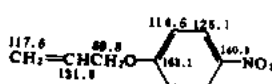
132



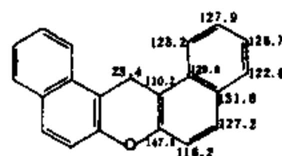
133. R = H
134. R = NO_2



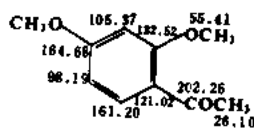
135[91]



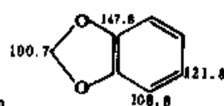
136[91]



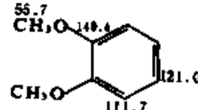
137[92] [$(CD_3)_2SO$]



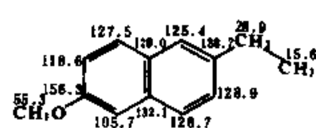
138[93]



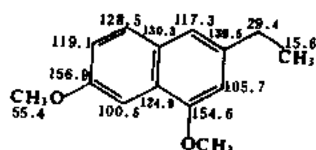
139[94]



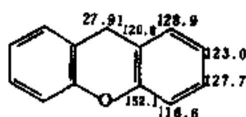
140[94]



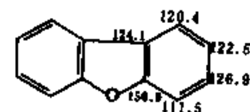
141[95]



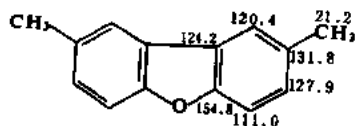
142[95]



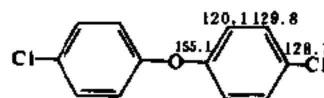
143[92] [$(CD_3)_2SO$]



144[96]



145[96]

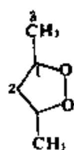


146[97]

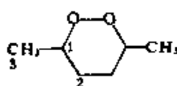
三、过氧化物的^{13}C-NMR化学位移

表 13-24　过氧化物 147～157 的^{13}C-NMR化学位移数据[79,88,98,99]

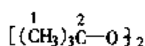
C \ 化合物	147	148	149	150	151	152	153	154	155	156	157
1	77.30	77.04	76.30	77.08	26.8	72.8	82.5	74.8	83.5	138.5	162.7
2	19.25	18.40	18.18	18.79	78.1	23.9	38.2	23.7	37.6	134.3	133.9
3	49.34	48.61	27.04	31.58						142.7	129.5
4											128.6
5											125.5
7										112.5	
9										37.6	
10										32.9	
R							28.1		27.6		



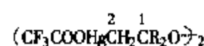
147. *cis*
148. *trans*



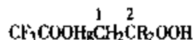
149. *cis*
150. *trans*



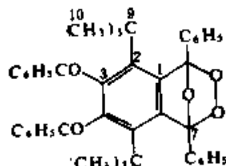
151



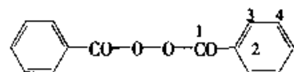
152. R = H
153. R = CH_3



154. R = H
155. R = CH_3



156



157

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第十四章　醛类和酮类化合物的¹³C-NMR 化学位移

醛和酮的¹³C-NMR 谱中羰基碳的化学位移的特征：

① 酮羰基在最低场，如果 α 碳的氢原子被烷基取代后，羰基碳的化学位移随着烷基数目的增加而移向低场；当酮的 α 位有卤素取代时，羰基碳的化学位移移向高场。

② α，β 不饱和酮的羰基碳的化学位移比饱和酮在高场，如果 α-烯碳上的氢被烷基取代，羰基信号移向低场，β-烯碳上的氢被烷基取代，羰基信号移向高场，若双键上有 3 个烷基取代使羰基碳向低场位移。

③ 芳香环与羰基共轭，使羰基受到屏蔽，芳环的间位和对位有取代基时，对酮羰基影响较小，若在邻位上有取代基时，则影响较大。

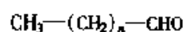
④ 环酮的羰基碳的化学位移受环的大小影响明显，环戊酮的羰基碳的化学位移在最低场，环丁酮和环己酮的羰基碳的化学位移在较高场。当 α 碳上有取代基时，羰基碳的化学位移出现在较低场，而 β 位的取代基影响不大。

⑤ 醛和酮的羰基碳的化学位移相似，一般情况下比酮向高场位移 5～10 个 δ 单位。

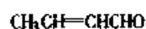
第一节　醛类化合物的¹³C-NMR 化学位移

表 14-1　醛类化合物 1～11 的¹³C-NMR 化学位移数据[1-4]

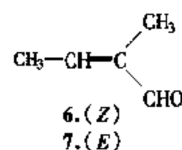
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
1	199.8	202.8	202.5	191.0	193.5	190.9	194.5	69.1	83.1	192.4	194.9
2	30.9	37.3	45.9			16.4	8.8	81.0	81.8		13.9
3		6.0	15.8			12.8	14.8	8.7	176.8		
4			13.8	13.9	18.4			27.7			
5								200.7			
6								14.4			



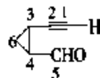
1. n = 0
2. n = 1
3. n = 2



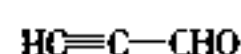
4. *cis*
5. *trans*



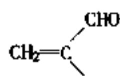
6. (Z)
7. (E)



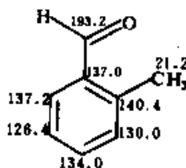
8



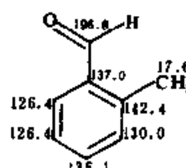
9



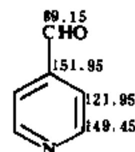
10. R = H
11. R = CH₃



12[5]



13[5]

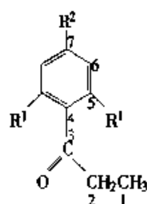
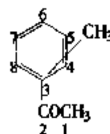
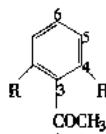
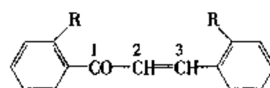
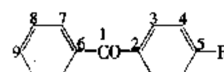


14[6] [D₂O]

第二节　酮类化合物的^{13}C-NMR 化学位移

表 14-2　芳酮类化合物 1～14 的^{13}C-NMR 化学位移数据[7～11]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	8.3	7.7	50.7	50.7	50.5	25.8	31.7	31.1	33.1	194.59	191.07	196.3	195.4	194.7
2	31.7	38.0	166.3	165.6	165.3	196.9	206.6	198.9	205.7	118.35	126.90	137.6	130.2	142.9
3	199.9	211.0	129.0	130.1	126.7	137.5	142.9	140.6	109.2	142.19	138.35	129.9	132.6	130.6
4	132.8	138.2	136.0	127.2	128.4	129.3	132.7	130.3	162.6			128.2	113.6	123.6
5	128.0	128.6	130.8	137.2	128.4	129.3	128.1	129.2	107.7			132.3	163.3	149.9
6	128.7	132.5	124.3	130.8	142.2	132.5	128.1	131.0	135.7			137.6	138.3	136.4
7	137.3	140.1	134.2	127.2								129.9	129.7	130.1
8			130.8	125.6								128.2	128.2	128.7
9												132.2	131.9	133.4
R^1		19.1												
R^2		21.2												

1. $R^1 = R^2 = H$
2. $R^1 = R^2 = CH_3$

3. 4-CH_3
4. 5-CH_3
5. 6-CH_3

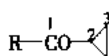
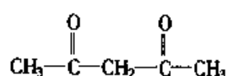
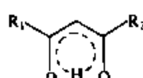
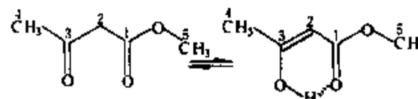
6. R = H
7. R = CH_3
8. R = Cl
9. R = OH

10. R = OH
11. R = $OCOCH_3$

12. R = H
13. R = OCH_3
14. R = NO_2

表 14-3　脂肪酮化合物 15～24 的^{13}C-NMR 化学位移数据[12～14]

C \ 化合物	15	16	17	18	19	20	21	22	23	24
1	199.1	207.2	29.7	23.7	191.5	191.9	200.9	167.89	173.19	168.11
2	17.0	21.0	202.3	191.7	100.6	95.5	90.4	49.72	89.73	91.03
3	11.3	10.4	57.8	100.2	191.5	200.2	200.9	200.25	176.33	173.46
4			202.3	191.7				29.70	20.89	18.78
5			29.7	23.7				51.91	55.29	50.52

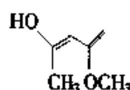
15. R = CH_3
16. R = C_6H_5

17. 酮式
18. 烯醇式

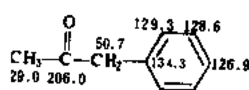
19. $R^1 = CH_3$，$R^2 = CH_3$
20. $R^1 = CH_3$，$R^2 = C(CH_3)_3$
21. $R^1 = R^2 = C(CH_3)_3$

22

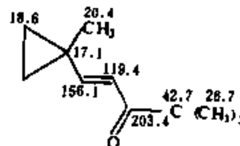
23



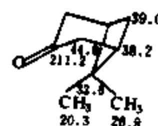
24



25[1]



26[15]



27[16]

表 14-4　α，β-不饱和酮 28～38 的 ^{13}C-NMR 化学位移数据[17-22]

C \ 化合物	28	29	30	31	32	33	34	35	36	37	38
1	198.1	198.5		28.9	90.9	96.7	113.71	28.8	27.2	10.2	10.6
2	137.5	144.5	193.8	199.3	121.8	119.5	143.40	197.5	196.4	36.0	29.5
3	128.6	125.2	97.6	126.9	196.8	189.2	50.33	94.0	97.0	200.2	200.3
4			153.4	148.9	40.5	50.2	220.71	155.5	152.2	94.2	98.6
5					30.9	32.7	120.69	35.3	29.9	152.9	154.9
6					23.0	29.1	155.60			37.3	36.9
7					22.1	22.0	20.82			45.2	45.0
8							27.81				
9							23.68				
R				55.5							

$CH_2=CRCOCH_3$（3 2 1）

28. R=H
29. R=CH_3

30. R=N $(CN_3)_2$
31. R=N$^\oplus$ $(CH_3)_3Cl^\ominus$

32. R=H
33. R=Br

34

$CH_3COCH=CHNHCH_3$（1 2 3 4 5）

35. *cis*
36. *trans*

表 14-5　α，β-不饱和酮和环酮化合物 39～54 的 ^{13}C-NMR 化学位移数据[23-26]

C \ 化合物	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
1	37.4 45.3	37.0 45.3	28.75	28.63	209.1	220.5	212.0	215.2	218.1	218.1	219.4	220.9	218.7	220.9	220.3	226.4
2	154.0	157.0	196.02	194.26	47.7	38.3	42.0	43.9	42.0	43.6	38.1	43.9	46.7	48.0	51.8	45.2
3	97.5	99.2	95.37	95.13	9.7	23.3	27.1	30.5	27.3	27.0	23.2	31.9	31.8	34.4	39.8	34.9
4	189.0	131.9	163.02	164.11			25.1	24.4	25.7	25.1		20.7	31.4	28.1	29.6	34.9
5			21.90	18.56					24.8	24.4		37.5	38.5	35.2	37.5	45.2
R				29.6												

37. *cis*
38. *trans*（$CHFCl_2$-71℃）

39. *cis*
40. *trans*

41. R=H
42. R=CH_3

43. $n=0$
44. $n=1$
45. $n=2$
46. $n=3$
47. $n=4$
48. $n=5$

49. R=H
50. R=2-CH_3
51. R=3-CH_3
52. R=*cis*-2,3-$(CH_3)_2$
53. R=*trans*-2,3-$(CH_3)_2$
54. R=2,2,5,5-$(CH_3)_4$

55[27]

56[28]

表 14-6 环酮化合物 57 ~ 69 的 ^{13}C-NMR 化学位移数据[27~29]

C \ 化合物	57	58	59	60	61	62	63	64	65	66	67	68	69
1	36.5	49.5	211.7	212.3	209.7	212.6	216.8	213.3	211.2	209.3	209.9	48.1	39.6
2	43.7	220.3	47.8	48.3	41.6	43.6	42.1	42.2	45.2	50.0	40.7	209.3	215.6
3	218.0	37.6	36.7	33.2	27.7	30.6	27.7	25.5	36.4	33.9	35.0	40.5	39.6
4		23.1	31.1	24.7	25.0	24.4	26.0	25.4	25.4	33.4	31.3	29.1	22.7
5			25.1	27.8			25.2	23.8	28.2	25.4		25.8	23.1
6			41.4	41.8				25.6	41.8	41.0		57.4	45.2
7			45.1	37.3					14.7	22.0	21.1	39.2	36.5
8			142.8	143.1								35.5	37.5
9			112.3	111.6									
10			22.0	22.1									

57

58

59. 3 位
60. 2 位

61. $n=0$
62. $n=1$
63. $n=2$
64. $n=4$

65. 2 位
66. 3 位
67. 4 位

68

69

70[30]

71[31]

72[32]

73[33]

74[34]

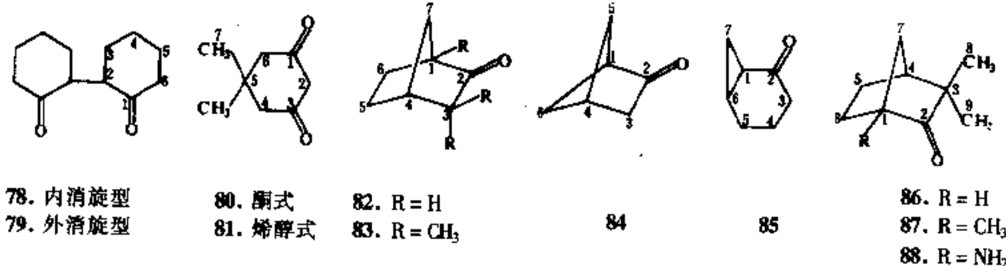
75[35]

76[36]

77[37]

表 14-7 环酮化合物 78 ~ 88 的 ^{13}C-NMR 化学位移数据[13,25,38~40]

C \ 化合物	78	79	80	81	82	83	84	85	86	87	88
1	211.5	210.6	204.6	191.4	50.3	53.7	56.0	25.7	50.0	53.8	68.96
2	49.4	50.4	58.2	103.7	217.7	219.3	214.0	208.7	222.0	222.6	221.67
3	30.3	29.2			45.6	46.9	40.8	36.6	46.8	43.1	46.61
4	25.7	25.1	54.9	47.2	36.2	45.5	35.8	17.9	46.1	45.3	42.02
5	28.2	26.7	33.6	31.6	27.8	25.1	40.9	21.3	23.3	24.9	24.93
6	42.4	41.9			24.9	31.8	40.9	17.4	24.5	31.8	32.04
7			29.1	29.1	38.1	41.6		10.2	34.7	41.5	43.39
8									21.4	21.6	21.72
9									23.2	23.3	23.49
R										14.6	



78. 内消旋型
79. 外消旋型

80. 酮式
81. 烯醇式

82. R = H
83. $R = CH_3$

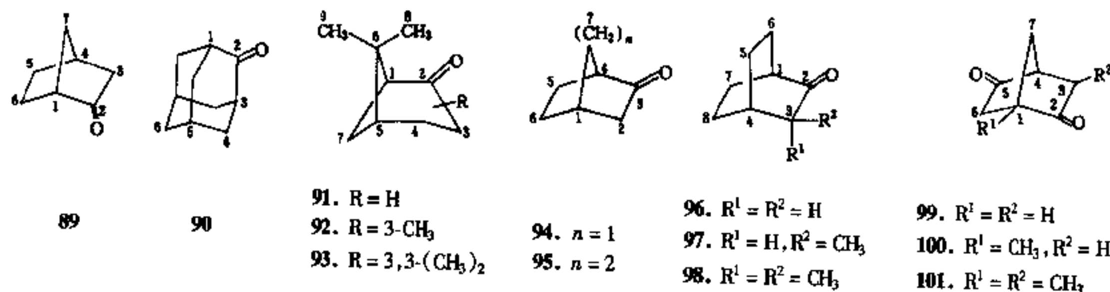
84

85

86. R = H
87. $R = CH_3$
88. $R = NH_2$

表 14-8 环酮化合物 89 ~ 101 的 ^{13}C-NMR 化学位移数据[1,25,41~43]

C \ 化合物	89	90	91	92	93	94	95	96	97	98	99	100	101
1	49.3	47.1	57.9	57.1	58.5	36.2	28.6	42.3	42.3	42.7	47.4	48.5	52.8
2	216.8	217.9	214.3	216.1	219.9	45.6	45.0	216.7	220.1	221.9	213.7	217.9	220.0
3	44.7		32.7	37.1	43.0	217.7	217.4	44.6	47.2	45.9	36.4	44.8	45.6
4	34.8	39.4	21.4	30.9	37.6	50.3	42.9	27.9	33.9	38.5	47.4	60.2	60.0
5	26.7	27.6	40.4	41.1	42.1	24.9	23.7	24.8	20.2	22.4	213.7	213.6	213.3
6	23.7	36.4	41.0	41.2	40.9	27.8	25.4	23.4	24.2	23.5	36.4	38.6	45.1
7	37.1		25.2	25.4	25.9	38.1	25.4	23.4	22.7	23.5	33.8	32.6	39.1
8			22.1	21.9	22.7			24.8	26.1	22.4			
9			25.8	26.3	26.4								
R^1				14.1	27.6					23.7		21.6	21.6
R^2					33.8				13.5	23.7			14.4



89

90

91. R = H
92. $R = 3\text{-}CH_3$
93. $R = 3,3\text{-}(CH_3)_2$

94. $n = 1$
95. $n = 2$

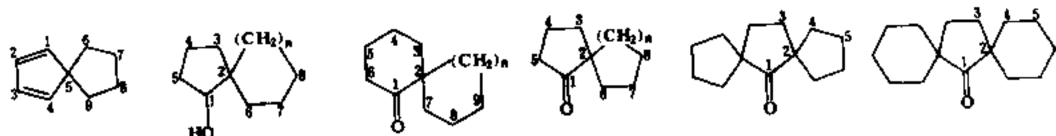
96. $R^1 = R^2 = H$
97. $R^1 = H, R^2 = CH_3$
98. $R^1 = R^2 = CH_3$

99. $R^1 = R^2 = H$
100. $R^1 = CH_3, R^2 = H$
101. $R^1 = R^2 = CH_3$

表 14-9 环酮化合物 102 ~ 110 的 ^{13}C-NMR 化学位移数据[44,45]①

C \ 化合物	102	103	104	105	106	107	108	109	110
1	143.89	79.7	80.2	212.1	214.0	221.3	221.0	225.8	223.9
2	128.64	55.4	46.5	57.4	49.2	56.7	49.7	59.1	50.5
3		38.7	35.3	40.5	39.5	38.7	35.3	36.2	31.2
4		20.2	20.0	23.5	21.2	20.2	20.0	37.9	33.6
5	64.64	37.3	38.0	27.9	28.0	37.3	38.0	26.6	22.8
6	32.95	36.9	33.3	39.6	38.7	36.9	33.3		26.5
7	26.66	26.4	23.5	35.9	34.4	26.4	23.5		
8		26.4	27.1	25.7	22.6		27.1		
9		36.9	23.5	25.7	26.9				
10			33.3	35.9	22.6				
11				34.4					
12									

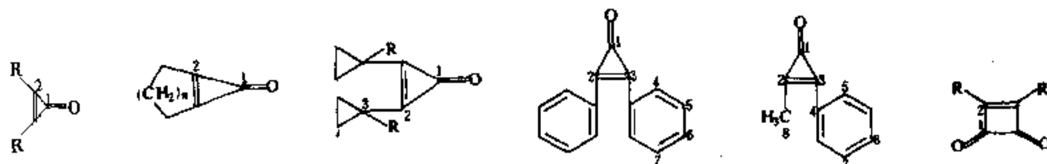
① 化合物 103 ~ 110 在二氧六环/六氟苯中测定。



102　　103. $n=1$　104. $n=2$　　105. $n=1$　106. $n=2$　　107. $n=1$　108. $n=2$　　109　　110

表 14-10　环酮化合物 111 ~ 121 的^{13}C-NMR 化学位移数据[46~49]

C \ 化合物	111	112	113	114	115	116	117	118	119	120	121
1	40.7	42.7	53.9	54.6	57.3	52.8	62.1	57.9	46.9	46.2	45.0
2	45.2	52.0	61.7	65.5	42.2	45.1	45.2	48.7	216.6	215.9	214.0
3	214.0	217.7	31.5	28.4	29.2	137.0	30.0	135.4	46.9	53.8	53.7
4	45.8	41.8	29.8	29.9	29.2	137.0	30.0	135.4	39.2	77.2	72.2
5	34.5	33.9	44.9	45.5	42.2	45.1	45.2	48.7	27.6	33.3	33.2
6			34.0	34.7	57.3	52.8	62.1	57.9	36.3	34.9	29.4
7			20.4	19.6	28.4	28.9	127.3	128.3	27.6	26.2	26.6
8			28.8	32.7	26.9	27.1	126.3	126.8	39.2	38.7	38.6
9			215.8	216.1	26.9	27.1	126.3	126.8	39.2	32.9	32.8
10					28.4	28.9	127.3	128.3	39.2	37.4	32.7



122. R = H
123. R = CH_3
124. R = $CH_2CH_2CH_3$
125. R = $C(CH_3)_3$

126. n = 2
127. n = 3

128. R = H
129. R = CH_3

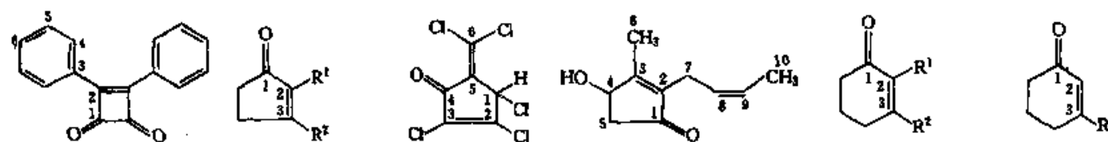
130

131

132. R = Cl
133. R = OCH_2CH_3

表 14-12 环酮化合物 134～146 的^{13}C-NMR 化学位移数据[17,50,52～54]

C \ 化合物	134	135	136	137	138	139	140	141	142	143	144	145	146
1	196.1	209.0	208.6	208.8	207.2	5.5	205.0	198.4	197.4	197.3	198.9	199.3	197.1
2	187.4	133.8	141.8	130.1	135.6	54.4	140.9	135.8	126.5	130.9	129.9	129.9	102.7
3	128.5	165.1	158.3	179.4	168.9	29.8	168.8	145.5	162.2	154.6	150.3	159.5	176.8
4	128.2					128.5	71.6						
5	129.4					47.3	44.3						
6	133.4					49.6	13.7						
7							20.9						
8							125.20						
9							125.79						
10							12.81						



134

135. $R^1 = R^2$ = H
136. $R^1 = CH_3, R^2$ = H
137. $R^1 = H, R^2 = CH_3$
138. $R^1 = R^2 = CH_3$

139

140

141. $R^1 = CH_3, R^2$ = H
142. $R^1 = H, R^2 = CH_3$
143. $R^1 = R^2 = CH_3$

144. R = H
145. R = C_6H_5
146. R = OC_2H_5

表 14-13 环酮化合物 147～156 的^{13}C-NMR 化学位移数据[21,55～57]

C \ 化合物	147	148	149	150	151	152	153	154	155	156
1	201.8	186.2	185.1	184.6	195.7	195.8	189.5	195.1	32.1	35.5
2	126.4	150.8	146.3	149.5	99.0	104.6	134.3	134.7	34.3	34.0
3	147.8	141.4	139.3	133.4	166.5	26.6	142.4	140.6	199.2	199.4
4	124.2	79.5	73.6	92.7	23.2	23.9	94.3	95.4	126.0	123.9
5	144.4	35.5	35.0	35.5	27.5	25.1	98.0	66.1	170.0	171.0
6	47.7	30.0	29.5	29.3	36.7	39.3	54.6	54.5	31.8	33.3
7		40.2	40.6	41.9	40.4	150.7	53.6	53.7	20.8	26.5
8		26.0	26.0	26.2		43.5	66.9	67.1	28.6	30.5
9							56.6	56.6	39.5	43.1
10									39.4	39.0
11									16.4	15.3
12									23.8	16.2
R							55.9			

147

148. R = OCH_3
149. R = Cl
150. R = NO_2

151

152

153. R = OCH_3
154. R = H

155

156

157[58]

158[58]

159[59]

160[60]

161[60]

162[61]

163[61]

164[62]

165[63] [$(CD_3)_2SO$]

166[63] [$(CD_3)_2SO$]

167[63] [$(CD_3)_2SO$]

168[64]

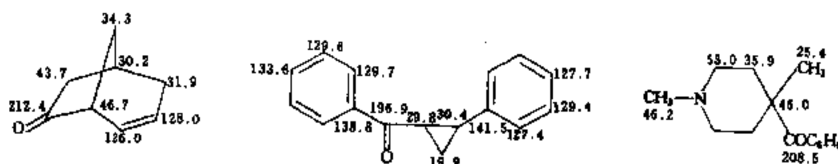
169[64]

170[65] [CCl_4]

171[66]

172[67]

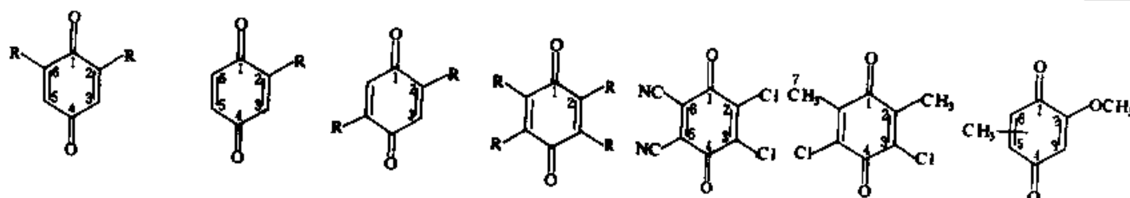
173[68]



174[69]　　　175[70]　　　176[71] [$CHFCl_2$]

表 14-14　苯醌类化合物 177 ~ 189 的^{13}C-NMR 化学位移数据[72]

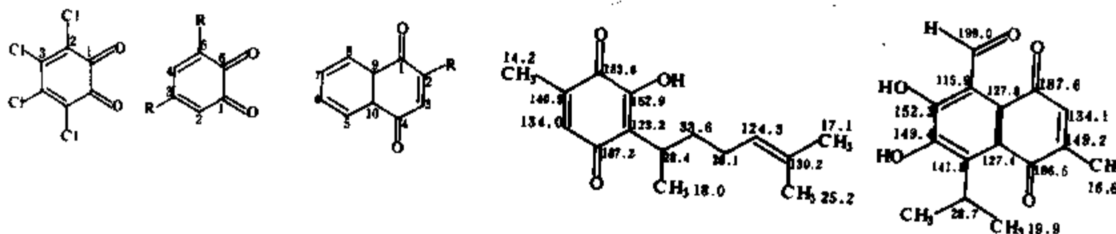
C \ 化合物	177	178	179	180	181	182	183	184	185	186	187	188	189
1	187.0	187.6	187.7	187.5	179.2	188.2	187.0	186.9	169.4	170.1	182.5	182.1	182.3
2	136.4	145.8	157.7	145.9	144.1	154.2	145.7	143.3	139.4	142.1	142.7	158.8	158.8
3		133.8	130.1	133.3	133.7	133.5	132.6			142.1	139.9	107.6	107.3
4		188.3	188.6	187.7	184.9					170.1	172.3	187.6	187.3
5				136.6	136.8					132.9		146.9	133.8
6				136.5	136.0							131.3	143.6
7											13.4		
R				15.8									



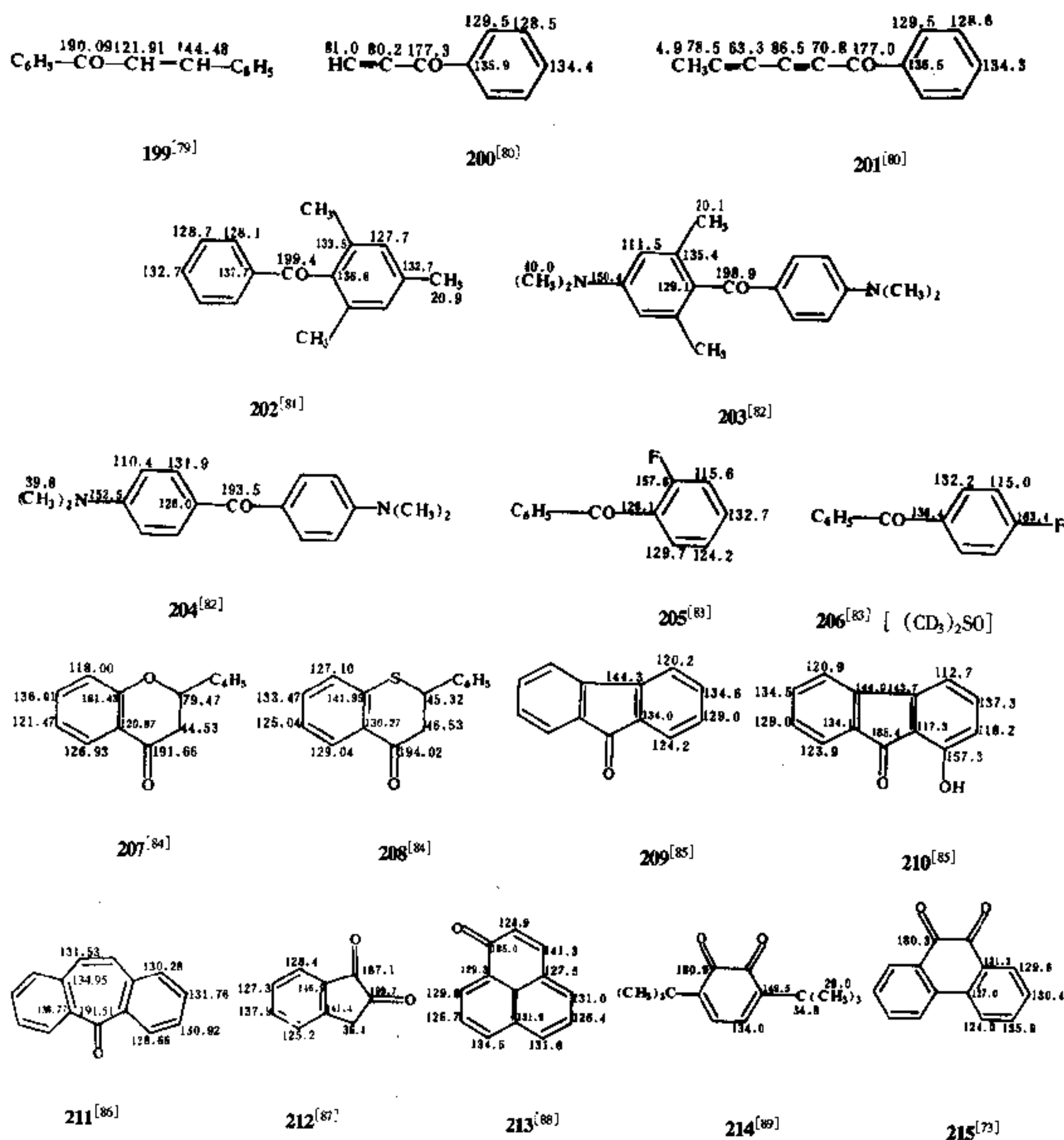
177. R = H
178. R = CH_3
179. R = C $(CH_3)_3$
180. R = CH_3
181. R = Cl
182. R = C $(CH_3)_3$
183. R = C_6H_5
184. R = C_6H_5
185. R = Cl
186
187
188. 5-CH_3
189. 6-CH_3

表 14-15　苯醌类化合物 190 ~ 196 的^{13}C-NMR 化学位移数据[72,74~76]

C \ 化合物	190	191	192	193	194	195	196
1	168.7	180.2	180.6	184.6	184.9	180.0	177.7
2	131.9	140.0	121.6	138.5	147.8	160.4	146.2
3		130.4	149.4		135.4	109.9	135.8
4			133.1		184.3	184.7	182.4
5			162.8	126.2	125.8	126.1	126.7
6			179.6	133.6	133.3	134.3	134.4
7					133.3	133.3	134.0
8					126.2	126.6	127.4
9				131.7	131.9	131.1	131.3
10					131.9	132.0	131.7
R					16.3	56.4	



190
191. R = H
192. R = C $(CH_3)_3$
193. R = H
194. R = CH_3
195. R = OCH_3
196. R = Cl
197[77]
198[78]



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88 Highet R J et al. J Magn Reson, 1975; 17: 336
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第十五章 有机酸、酸酐及酯类化合物的^{13}C-NMR化学位移

有机酸及其酯的羰基碳的化学位移有如下一些特征。

① 有机酸中羧基的羰基碳的化学位移比酮和醛羰基碳的化学位移在较高场，其范围一般在161～186，相应的阴离子向低场位移3～5个δ单位。

② 在有机酸中，羧基使烷基部分的α、β、δ位碳的化学位移移向低场，使γ位碳移向高场。

③ α、β不饱和的有机酸和饱和酸比较，α、β不饱和有机酸的羰基碳的化学位移向高场位移了(8～10)个δ单位。

④ 酯中的羰基碳的化学位移范围在(163～179)个δ单位，羧酸部分对羰基碳的化学位移影响较大，而醇部分影响较小。

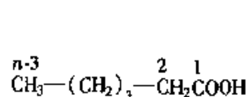
第一节 有机酸及酸酐类化合物的^{13}C-NMR化学位移

一、有机酸类化合物的^{13}C-NMR化学位移

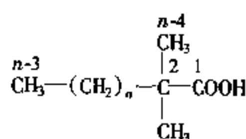
表 15-1 脂肪有机酸 1～17 的^{13}C-NMR化学位移数据[1～3]①

C \ 化合物①	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	179.6	180.8	185.5	184.6	185.3	39.82	41.85	11.73	9.53	176.4	164.3	158.9	160.0	162.5	160.8	155.9	159.5
2	36.3	34.4	42.7	41.9	42.3	36.29	32.46	27.16	33.72	30.0	114.5	115.8	107.0	108.8	109.1	109.1	108.9
3	18.5	24.8	33.5	42.8	40.6	20.71	29.57	41.58	42.99		39.6		118.8	109.2		111.0	111.4
4	13.4	31.8	9.3	18.1	27.4	14.15	11.43	16.80	24.82		168.0			118.3			
5		22.8	24.6	14.5	25.1	17.22	19.34										
6		14.1		24.9	14.1												
7					23.5												

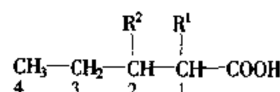
① 化合物6～9在D_2O中测定，10～17在二氧六环中测定。



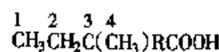
1. $n=1$
2. $n=3$



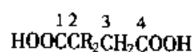
3. $n=1$
4. $n=2$
5. $n=3$



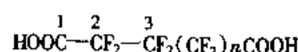
6. $R^1=CH_3$，$R^2=H$
7. $R^1=H$，$R^2=CH_3$



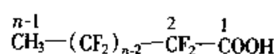
8. R＝H
9. $R=CH_3$



10. R＝H
11. R＝F



15. $n=0$
16. $n=1$
17. $n=2$

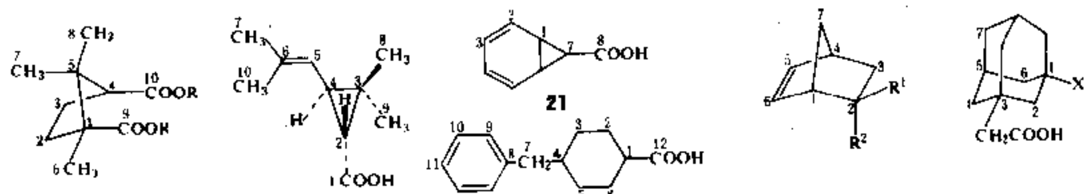


12. $n=1$
13. $n=2$
14. $n=3$

表 15-2 脂肪有机酸 18 ~ 28 的 ^{13}C-NMR 化学位移数据[4~9]①

C \ 化合物	18	19	20	21	22	23	24	25	26	27	28
1	56.66	56.20	179.4	119.7	129.8	39.2	46.8	45.7	34.3	68.5	60.9
2	33.19	32.16	34.6	126.1	141.7	27.2	43.3	43.4	45.6	50.0	53.9
3	23.12	22.58	29.8	131.8	32.3	120.8	30.4	29.2	33.2	35.8	37.3
4	53.04	52.79	33.6		34.5	137.1	41.7	42.6	41.4	41.4	40.6
5	46.63	46.88	120.8		23.7	27.5	138.2	137.9	28.7	30.8	32.9
6	21.99	21.60	135.8		27.9	25.3	135.8	132.5	40.1	44.3	49.0
7	21.51	21.08	25.6	45.0	42.4	44.1	46.5	49.7	35.9	35.8	35.1
8	23.12	22.58	22.3	180.9	140.3	140.3					
9	175.66	180.26	20.4		129.1	128.9					
10	177.55	182.25	18.5		128.3	128.3					
11					126.0	126.0					
12					172.9	182.6					
R							183.1	181.3			

① 化合物 26 ~ 28 在 CCl_4 中测定。



18. R = H
19. R = OH

20

21

22. Δ^1
23. Δ^3

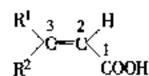
24. R^1 = COOH, R^2 = H
25. R^1 = H, R^2 = COOH

26. X = CH_2Br
27. X = OH
28. X = Br

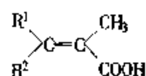
表 15-3 烯酸化合物 29 ~ 41 的 ^{13}C-NMR 化学位移数据[10,11]

C \ 化合物	29	30	31	32	33	34	35	36①	37①	38	39	40	41
1	168.9	166.5	169.3	166.2	170.8	171.3	170.9	162.8	162.8	172.2	172.1	171.8	171.8
2	129.2	124.7	122.8	117.1	136.3	127.4	128.2	121.3	119.5	119.8	120.8	118.8	119.0
3	130.8	122.0	146.0	146.4	126.2	136.6	137.9	144.6	133.5	152.8	151.6	154.3	152.3
4					17.5	15.2	11.1			24.9	34.2	22.6	30.7
5										11.4	21.1	13.0	21.8
6											13.3		12.9
R			17.3	27.3		19.9	13.5	24.1	24.9				

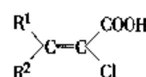
① 化合物 36,37 在 $(CH_3)_2SO$ 中测定。



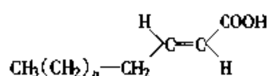
29. $R^1 = R^2$ = H
30. R^1 = H, R^2 = Br
31. R = CH_3, R^2 = H
32. R^1 = CH_3, R^2 = Cl



33. $R^1 = R^2$ = H
34. R^1 = H, R^2 = CH_3
35. R^1 = CH_3, R^2 = H

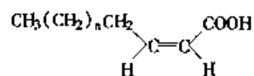


36. R^1 = CH_3, R^2 = Cl
37. R^1 = Cl, R^2 = CH_3



38. $n=0$

39. $n=1$



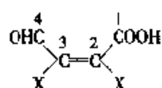
40. $n=0$

41. $n=1$

表 15-4 烯酸和芳酸化合物 42～51 的 ^{13}C-NMR 化学位移数据[11～15]

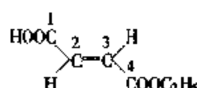
C \ 化合物①	42①	43①	44	45	46	47	48	49	50	51①
1	163.6	164.9	170.20	180.23	167.4	166.9	172.9	172.6	172.2	141.0
2	122.5	117.3	132.73	35.35	130.8	134.5	113.2	105.2	112.7	130.0
3	150.0	147.3	135.86	29.17			151.1	164.9	156.2	146.4
4	97.4	100.0	164.83	141.14			146.6	103.3	118.7	124.5
5				129.88			121.4	164.8	124.9	129.4
6				173.28			119.6	108.7	149.9	136.3
7							121.4	133.0	115.6	167.4
8										168.3
9										71.8
10										68.6
11										31.0

① 化合物 42,43,51 在 $(CD_3)_2SO$ 中测定，化合物 48～50 在 $(CD_3)_2CO$ 中测定。

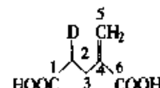


42. X＝Cl

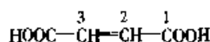
43. X＝Br



44

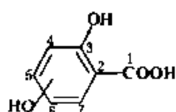


45



46. 顺式

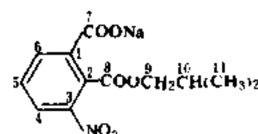
47. 反式



48. 4-OH

49. 5-OH

50. 6-OH



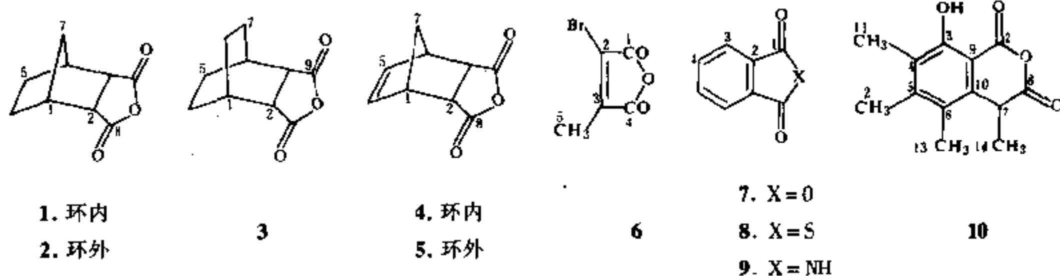
51

二、酸酐类化合物的 ^{13}C-NMR 化学位移

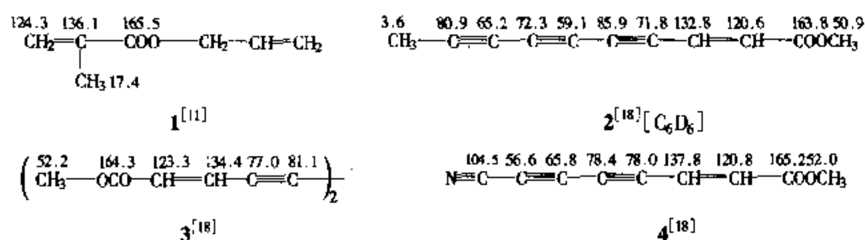
表 15-5 酸酐类化合物 1～10 的 ^{13}C-NMR 化学位移数据[8,11,16,17]

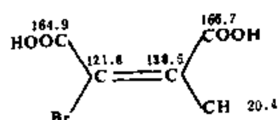
C \ 化合物	1	2	3	4	5	6①	7	8	9	10
1	40.2	41.0	26.1	47.2	48.8	164.0	162.6	189.9	167.6	
2	50.0	49.1	44.3	46.1	46.9	146.0	131.1	138.6	132.5	166.94
3						126.2	125.6	123.6	123.5	159.42
4						161.1	136.0	134.9	134.1	124.84
5	25.0	27.4	21.5	135.6	138.0	11.4				148.62
6										125.20
7	42.3	34.3	24.2	52.8	44.1					39.29
8	172.6	173.5		171.5	171.6					169.37
9			174.1							101.97
10										
11										12.47
12										18.12
13										15.14
14										22.91

① 化合物 6 在 $(CD_3)_2SO$ 中测定。

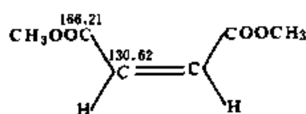


第二节 酯类化合物的^{13}C-NMR 化学位移

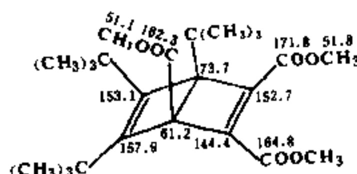




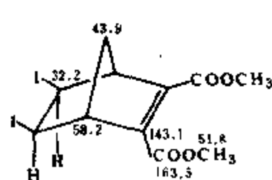
5[11][$(CD_3)_2SO$]



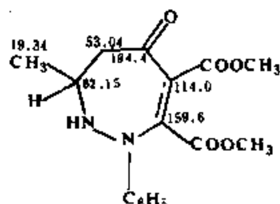
6[12][$(CD_3)_2SO$]



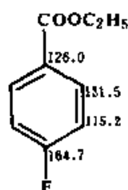
7[20]



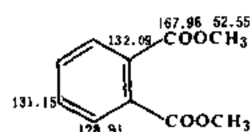
8[21][C_6D_6]



9[19]



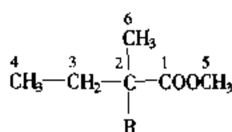
10[22]

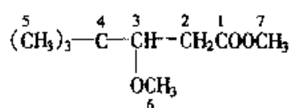


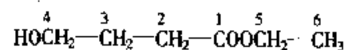
11[23]

表 15-6 有机酸酯类化合物 12~20 的^{13}C-NMR 化学位移数据[1,24~26]

C \ 化合物	12	13	14	15	16	17	18	19	20
1	176.2	177.3	173.5	174.5	64.3	64.2	69.7	174.2	61.9
2	41.4	43.0	36.2	31.1	131.7	124.7	130.4	32.9	35.2
3	27.6	33.9	86.3	27.9	117.1	130.0	123.1	39.6	29.2
4	11.4	9.4	35.7	61.8				44.9	36.8
5	51.1	51.3	25.9	60.6				65.2	25.4
6	16.8	24.9	60.2	14.2				29.7	124.4
7			51.6					26.0	130.4
8								26.0	25.1
9								27.2	19.2
10								60.3	17.3
11								14.2	
R^1						16.9	12.7		
R^2							12.3		

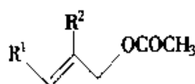


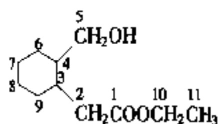


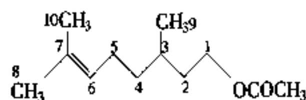


12. R = H　　14　　15

13. R = CH_3







16. $R^1 = R^2 = H$　　19　　20

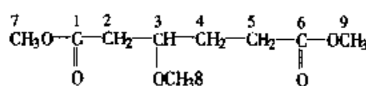
17. $R^1 = CH_3, R^2 = H$

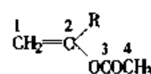
18. $R^1 = R^2 = CH_3$

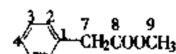
表 15-7　有机酸酯类化合物 21～30 的 ^{13}C-NMR 化学位移数据[27,28,30～34]

C \ 化合物	21	22	23	24	25	26	27	28	29	30①
1	173.7	96.6	101.2	136.1	51.9	18.89	63.7	89.5	38.6	150.9
2	29.7	141.2	152.8	128.5	73.9	20.64	164.4	161.9	50.3	121.4
3	76.6	166.1	167.4	128.5	69.8	30.03	53.5	52.3	88.3	129.0
4	38.9	20.1	20.5	128.1	169.6	45.15			52.2	125.3
5	29.1				20.2	53.17			51.7	
6	171.5								168.9	
7	51.5			20.7					53.1	
8	57.1			170.6						
9	51.5			66.1						
R			19.3							

① 化合物 30 在 $CCl_4 + CDCl_3$ 中测定。

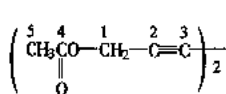


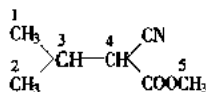


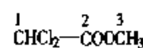


21　　22. R = H　　24

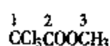
23. R = CH_3

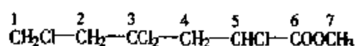


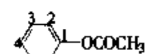




25　　26　　27





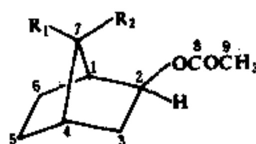


28　　29　　30

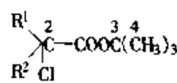
表 15-8　有机酸酯类化合物 31 ~ 44 的^{13}C-NMR 化学位移数据[35~38]

C \ 化合物	31	32	33	34	35	36	37	38	39	40	41	42	43①	44①
1	41.6	45.6	45.5	166.2	163.3	160.2	175.04	175.47	178.8	178.4	165.9	164.0	41.50	45.63
2	77.5	78.2	78.5	41.9	65.4	90.9	42.61	41.70	38.7	38.7	130.9	136.3	168.18	171.33
3	39.7	40.7	37.3	82.9	84.9	86.7			27.3	27.2	129.4	130.5	61.28	61.16
4	35.5	39.5	40.7	27.9	27.6	27.4			51.5	60.2	132.5	123.4	13.72	13.59
5	28.3	25.3	28.6				14.94	13.57			128.2	150.4		
6	24.2	22.0	26.2								68.2	69.7		
7	35.3	40.4	43.9				51.73	51.57			21.9	21.8		
8	170.5	170.5	170.6											
9	21.2	21.3	21.4											
R		11.7	13.0							14.2				13.11

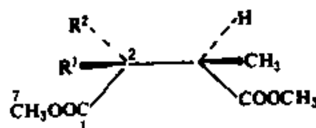
① 化合物 43 ~ 44 在$(CD_3)_2SO$中测定。



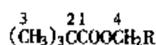
31. $R^1 = R^2 = H$
32. $R^1 = CH_3, R^2 = H$
33. $R^1 = H, R^2 = CH_3$



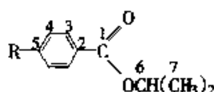
34. $R^1 = R^2 = H$
35. $R^1 = H, R^2 = Cl$
36. $R^1 = Cl, R^2 = H$



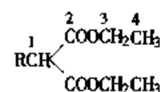
37. $R^1 = CH_3, R^2 = H$
38. $R^1 = H, R^2 = CH_3$



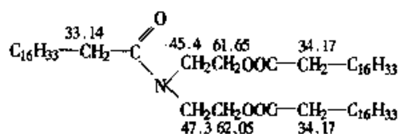
39. R = H
40. $R = CH_3$



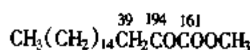
41. R = H
42. $R = NO_2$



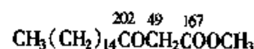
43. R = H
44. $R = CH_3$



45



46



47

表 15-9　有机酸酯类化合物 48 ~ 60 的^{13}C-NMR 化学位移数据[25,39~42]

C \ 化合物	48	49	50	51	52	53	54	55	56	57	58	59	60
1	51.5	51.4	51.4	61.4	61.6	47.4	42.7	46.1	44.2	33.8	31.3	33.7	30.5
2	175.2	175.7	177.0	72.2	72.9	29.1	26.4	28.3	26.4	44.2	42.6	44.3	43.6
3	12.7	37.9	43.7	70.7	71.2	24.3	24.0	26.5	26.4	29.5	28.6	31.6	29.6
4	8.3	25.2	30.0	68.3	68.8			28.7	27.1		25.0	26.2	24.1
5		18.4	25.8	226.6	229.1	174.1	173.9	174.5	175.0				26.8
6				48.8	55.7	51.4	51.5	51.4	51.6	175.3	175.3	176.0	176.8
7				28.3	33.8					51.5	51.6	51.4	51.6
8				18.1	26.0								

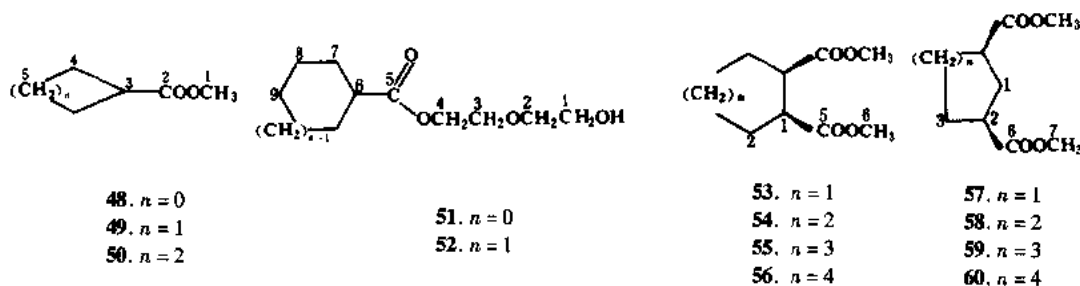
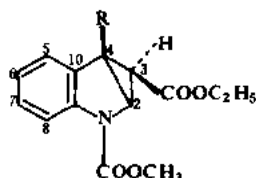
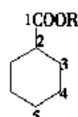


表 15-10 有机酸酯类化合物 61～69 的^{13}C-NMR 化学位移数据[10,41,43,44]

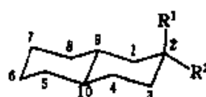
C \ 化合物	61	62	63	64	65	66	67	68	69
1			182.1	175.3	34.6	36.3	166.0	167.1	164.4
2	45.0	49.3	43.7	43.4	39.1	42.6	128.7	128.3	132.4
3	24.1	28.8	29.6	29.6	27.3	29.1	129.9	137.9	126.8
4	28.2	33.7	26.2	26.0	30.2	33.1	50.9	50.3	52.0
5	124.1	122.6	26.6	26.4	33.8	33.8			119.1
6	122.4	122.4			26.5	26.6		20.5	17.0
7	127.4	127.4			26.4	26.6		20.5	
8	115.1	115.0			33.6	33.7			
9	140.8	140.1			39.5	42.4			
10	130.0	134.8			43.1	43.4			



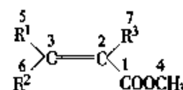
61. R = H
62. R = CH_3



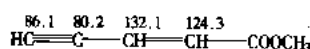
63. R = H
64. R = CH_3



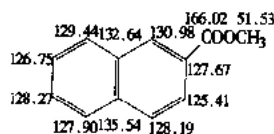
65. $R^1 = COOCH_3, R^2 = H$
66. $R^1 = H, R^2 = COOCH_3$



67. $R^1 = R^2 = R^3 = H$
68. $R^1 = H, R^2 = R^3 = CH_3$
69. $R^1 = CN, R^2 = CH_3, R^3 = H$



70[18]

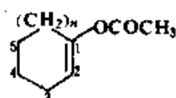


71[29]

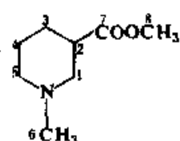
表 15-11 有机酸酯类化合物 72～80 的^{13}C-NMR 化学位移数据[14,28,36,45]

C \ 化合物	72	73	74	75	76	77①	78①	79	80
1	148.4	150.3	57.2	146.1	52.9	167.0	171.0	165.9	164.0
2	113.0	115.3	46.3	93.4	128.9	131.0	113.4	130.9	136.3
3	21.5	24.5	23.7	19.3	136.2	130.0	162.4	129.4	130.5
4	23.5	29.3	26.1	20.8	26.2	129.0	118.4	132.5	123.4
5	22.5	25.5	55.5	47.3	50.5	133.4	136.3	128.2	150.4
6	27.0	27.5	41.2	42.3	45.3		120.0	68.2	69.7
7		26.0	173.3	168.4	164.6		130.6	21.9	21.8
8		29.3	50.9	49.8	50.5	52.3	52.4		

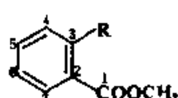
① 化合物 77,78 在$(CD_3)_2CO$中测定。



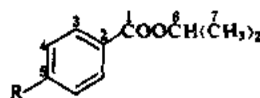
72. n = 1
73. n = 3



74. —
75. Δ^2
76. Δ^3



77. R = H
78. R = OH

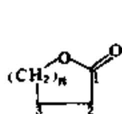


79. R = H
80. R = NO_2

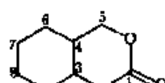
第三节　内酯类化合物的^{13}C-NMR 化学位移

表 15-12　内酯类化合物 1～10 的^{13}C-NMR 化学位移数据[26,46,47]

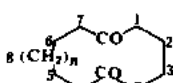
C \ 化合物	1	2	3	4	5	6	7	8	9	10
1	178.1	171.2	171.4	41.7	41.3	28.8	26.9	46.2	39.1	53.8
2	27.8	29.8	37.4	20.9	22.1	20.1	22.9	36.7	30.2	87.7
3	22.3	19.1	36.5	64.2	64.1	65.1	64.6	34.0	35.8	43.2
4	68.8	22.7	38.2	34.5	34.9	34.9	34.0	46.4	46.9	44.6
5		69.4	74.7	26.7	24.4	25.3	24.8	30.8	33.2	29.1
6			32.5	22.8	22.3	24.5	23.1	88.1	91.4	21.3
7			25.3	39.0	40.2	31.9	29.9	37.0	38.3	30.3
8			25.3		26.2		26.5	178.3	168.0	176.0
9			27.2						33.1	26.8
10										36.4



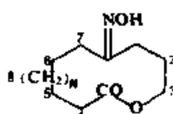
1. n = 1
2. n = 2



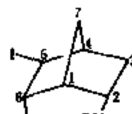
3



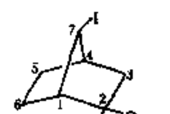
4. n = 0
5. n = 1



6. n = 0
7. n = 1



8. n = 0
9. n = 1



10

表 15-13　内酯类化合物 11～18 的^{13}C-NMR 化学位移数据[21,48～50]

C \ 化合物	11①	12	13	14	15	16	17	18
1	31.6	23.78	27.01	38.95	174.8	173.6	172.3	169.18
2	36.7	77.97	76.67	23.06				120.91
3	36.9	35.26	35.39	81.89				156.60
4	55.5	26.36	30.69	33.95	155.8	161.9	166.0	88.62
5	82.5	40.93	43.00	50.49	89.0	87.5	85.7	24.90
6	33.2	28.12	34.95	21.31				
7	29.1	21.52	20.51	21.47				
8	168.5	21.87	21.59	26.65				
9	170.3		18.12	44.37				
10	51.8			33.66				
11				19.45				
12				11.87				
13				53.83				
14				153.28				

① 化合物 11 在 C_6D_6 中测定。

11　　12　　13　　14

15. $R^1 = R^2 = H$

16. $R^1 = H, R^2 = CH_3$

17. $R^1 = R^2 = CH_3$

18

表 15-14　内酯类化合物 19～26 的^{13}C-NMR 化学位移数据[52～54]

C \ 化合物	19	20	21	22	23	24	25	26
1	153.7	171.1	170.4	168.7	171.4	171.7		
2							174.0	174.1
3	97.6		69.5	68.5	69.6	71.8	32.5	32.7
4	148.4	151.7	146.3	139.6	134.4	139.4	123.3	122.9
5	161.9	90.8	122.0	116.7	123.0	115.1	122.4	118.9
6	158.6		133.6	119.9	121.0	114.7	133.7	146.8
7			128.5	152.6	149.8	149.5	126.2	122.7
8			124.9	148.6	107.3	145.6	133.1	133.3
9			125.2	118.1	125.9	108.0	150.5	150.4
10						103.8		

19　　20

21. R = H

22. $R = OCH_3$

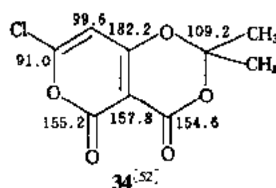
23　　24

25. $R^1 = CH_3$, $R^2 = C(CH_3)_3$

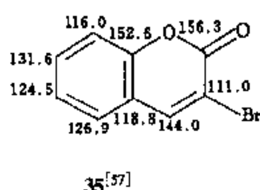
26. $R^1 = R^2 = C(CH_3)_3$

27[55]　　28[55]　　29[55]　　30[56][$(CD_3)_2SO$]

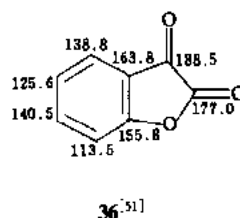
31[56][$(CD_3)_2SO$]　　32[52]　　33[52]



34[52]



35[57]



36[51]

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53 Hughes D W et al. Can J Chem, 1976;54:2252
54 Becker H-D et al. J Org Chem, 1977;42:2966
55 -Pelter A et al. J Chem Soc Perkin I, 1976;2475
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57 Cussans N J et al. Tetrahedron, 1975;31:2591
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59 Hansen P E et al. Org Magn Reson, 1977;9:649

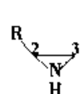
第十六章　杂环化合物的^{13}C-NMR化学位移

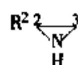
第一节　三元及四元杂环化合物的^{13}C-NMR化学位移

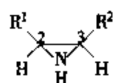
一、三元杂环化合物的^{13}C-NMR化学位移

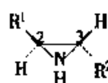
表 16-1　三元杂环化合物 1～18 的^{13}C-NMR化学位移数据[1]

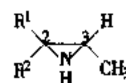
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		
2	18.2	25.1	39.7	31.6	30.2	43.9	29.2	37.1	39.9	33.5	40.4	43.7	35.1	41.0	48.7	40.3	47.0	54.8
3		25.8	21.4	29.2	32.5	35.3		32.1			37.0		37.8	39.0	38.7		40.8	42.2
4																22.4	23.5	23.8

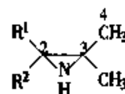












1. R = H　**2.** R = CH_3　**3.** R = $C(CH_3)_3$　**4.** R = C_6H_5

5. R = CH_3　**6.** R = C_6H_5

7. $R^1 = R^2 = CH_3$　**8.** $R^1 = C_6H_5, R^2 = CH_3$　**9.** $R^1 = R^2 = C_6H_5$

10. $R^1 = R^2 = CH_3$　**11.** $R^1 = C_6H_5, R^2 = CH_3$　**12.** $R^1 = R^2 = C_6H_5$

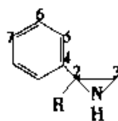
13. $R^1 = R^2 = CH_3$　**14.** $R^1 = C_6H_5, R^2 = CH_3$　**15.** $R^1 = R^2 = C_6H_5$

16. $R^1 = R^2 = CH_3$　**17.** $R^1 = C_6H_5, R^2 = CH_3$　**18.** $R^1 = R^2 = C_6H_5$

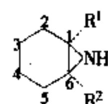
表 16-2　三元杂环化合物 19～33 的^{13}C-NMR化学位移数据[2～5,7]

C \ 化合物	19①	20①	21	22	23	24	25	26	27	28①	29①	30	31	32	33
1			28.8	34.9	39.9										
2	36.3	44.0	25.1	30.6	32.0	28.65	31.93	39.32	33.27					75.3	81.1
3			20.5	20.5	21.3	160.60	165.87	163.19	164.16	65.5	84.3	81.6	84.3		
4	143.9	143.2		20.6						58.1	40.7	48.5	40.7	72.4	78.2
5	126.0	128.0		24.9						25.1	27.6	135.5	27.6		
6	128.2	128.5		37.8								128.4	24.9	46.2	52.1
7	126.5	127.2										127.9	25.7		
8												130.0	25.2		
9											36.5		36.5		
R	24.8			27.1	22.7		21.67	1	12.52						

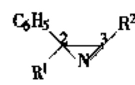
① 化合物 19～20 在 CD_2Cl_2 中测定，化合物 28～29 在 CH_2Cl_2 中测定。



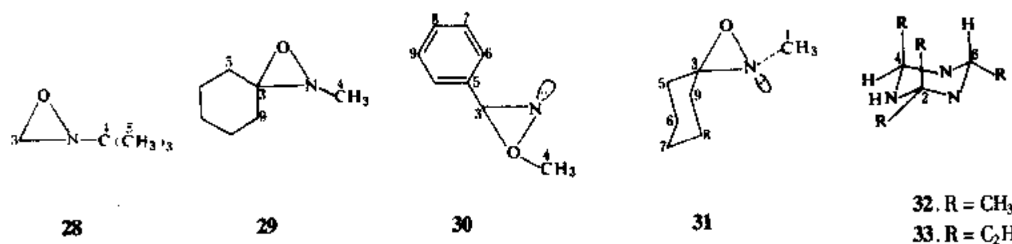
19. R = CH_3
20. R = C_6H_5



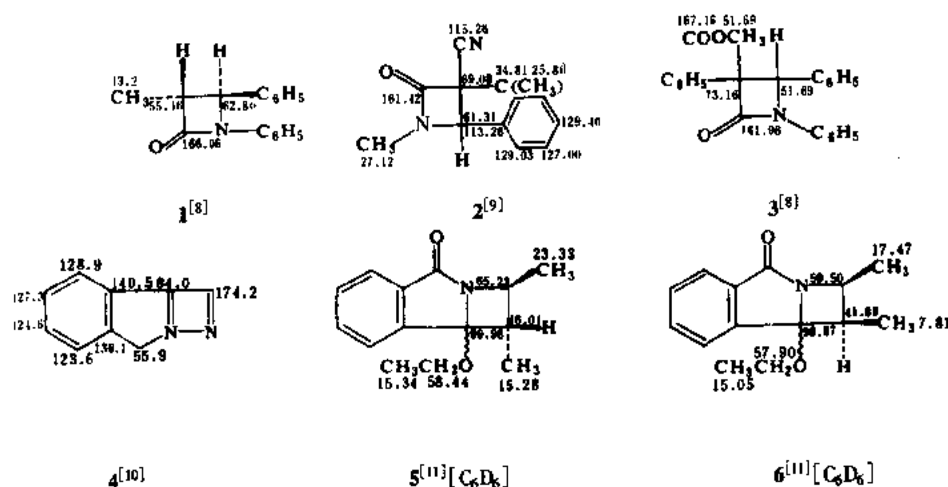
21. $R^1 = R^2 = H$
22. $R^1 = CH_3, R^2 = H$
23. $R^1 = R^2 = CH_3$



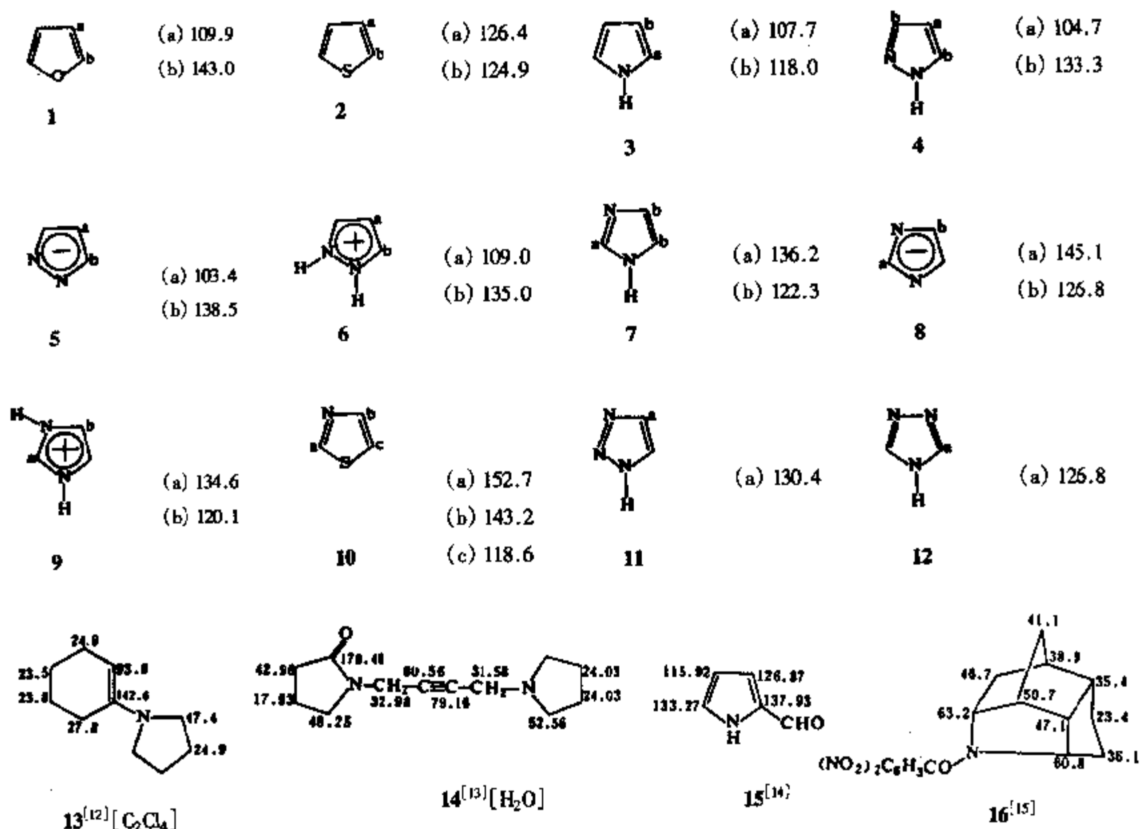
24. $R^1 = R^2 = H$
25. $R^1 = CH_3, R^2 = H$
26. $R^1 = C_6H_5, R^2 = H$
27. $R^1 = H, R^2 = CH_3$

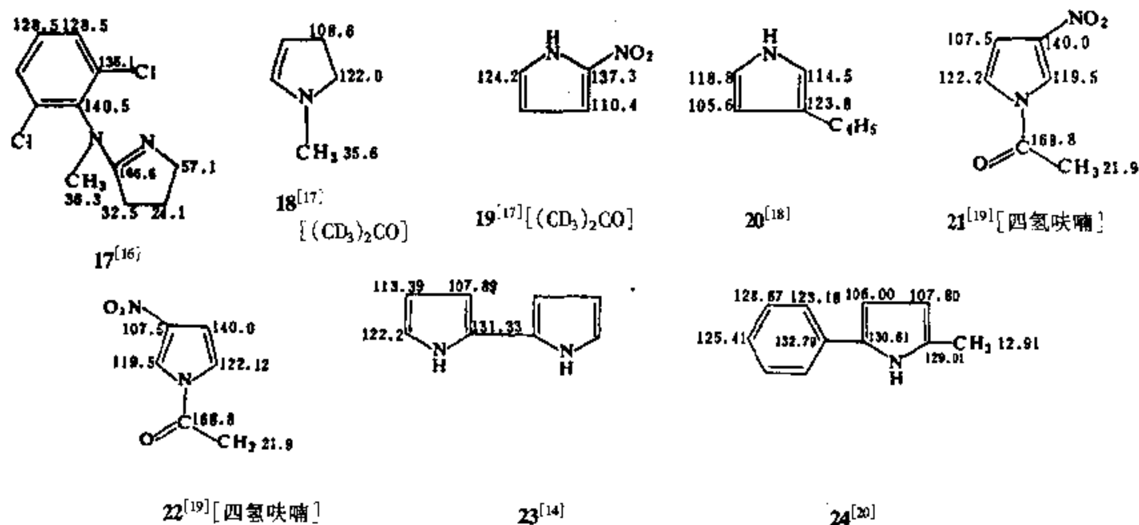


二、四元杂环化合物的^{13}C-NMR 化学位移



第二节　五元杂环化合物的^{13}C-NMR 化学位移





17[16]

18[17] [$(CD_3)_2CO$]

19[17] [$(CD_3)_2CO$]

20[18]

21[19] [四氢呋喃]

22[19] [四氢呋喃]

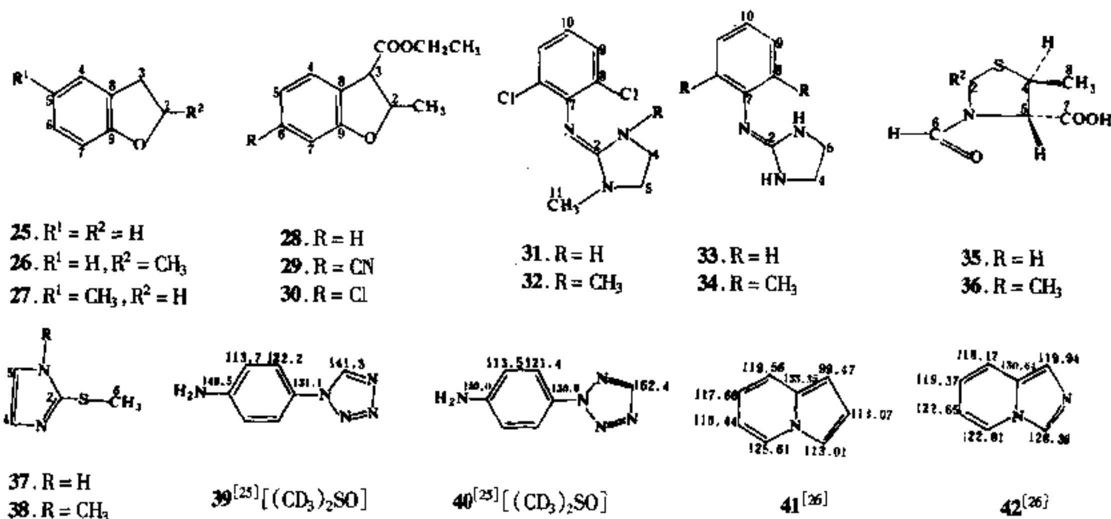
23[14]

24[20]

表 16-3　五元氧杂环和氮杂环化合物 25～38 的 ^{13}C-NMR 化学位移数据[16,21～24]①

C ＼ 化合物	25	26	27	28	29	30	31	32	33	34	35	36	37	38
2	145.1	155.9	145.4	165.8	169.0	166.1	155.9	155.1	158.3	156.2	49.0	70.7	140.5	141.7
3	106.9	104.0	107.1	109.8	108.6	109.7								
4	121.6	121.2	121.9	139.5	139.6	139.7	40.3	48.3	42.6	42.4	65.2	69.2	123.6	128.3
5	123.2	123.5	132.5	146.8	147.2	144.6	49.4	48.3			45.0	41.7	123.6	122.5
6	124.6	124.2	126.4	101.2	88.8	107.8					161.6	160.4	15.9	15.7
7	111.8	111.7	111.7	132.4	143.8	140.4	145.2	145.6	150.0	147.6	171.0	171.2		
8	127.9	130.2	128.4	117.8	122.8	115.8	129.2	128.2	122.7	130.7	21.1	20.0		
9	155.5	155.7	154.1	137.4	137.0	138.6	128.1	127.5	128.9	127.7				
10							122.3	120.6	121.3	127.7				
11							32.5	33.9						
12														
R		14.7	22.0									31.0		
										18.2		33.0		

① 化合物 25～27 在 CS_2 中测定，37～38 在 $(CD_3)_2SO$ 中测定。



25. $R^1 = R^2 = H$
26. $R^1 = H, R^2 = CH_3$
27. $R^1 = CH_3, R^2 = H$

28. R = H
29. R = CN
30. R = Cl

31. R = H
32. R = CH_3

33. R = H
34. R = CH_3

35. R = H
36. R = CH_3

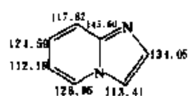
37. R = H
38. R = CH_3

39[25] [$(CD_3)_2SO$]

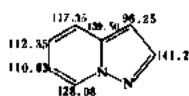
40[25] [$(CD_3)_2SO$]

41[26]

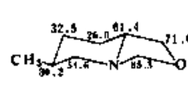
42[26]



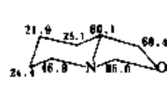
43[26]



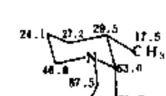
44[26]



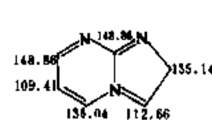
45[27]



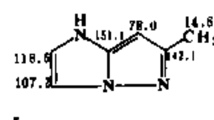
46[27]



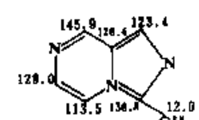
47[27]



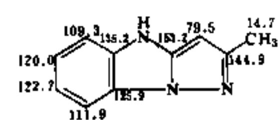
48[26]



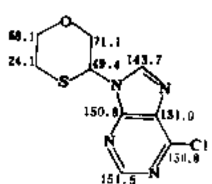
49[28]



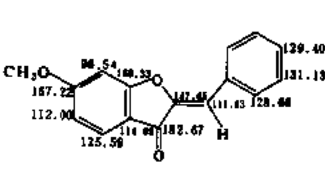
50[29]



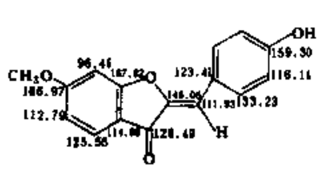
51[28] [$(CD_3)_2SO$]



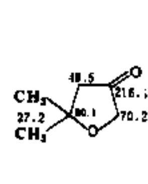
52[30]



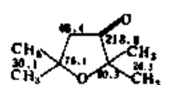
53[31]



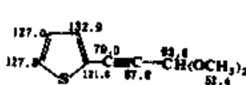
54[31]



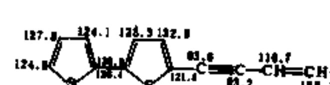
55[32]



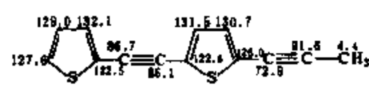
56[32]



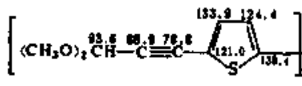
57[33]



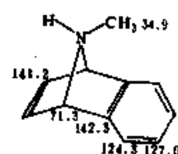
58[33]



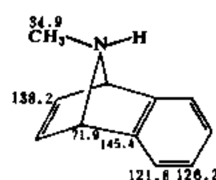
59[33]



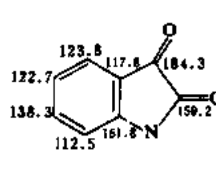
60[33]



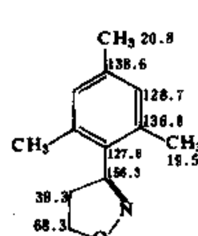
61[34]



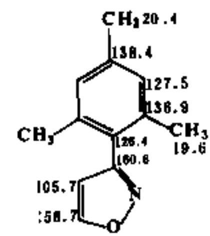
62[34]



63[35] [$(CH_3)_2SO$]



64[36]



65[36]

表 16-4 五元氧杂环化合物 66 ~ 79 的^{13}C-NMR 化学位移数据[20,37,38]①

C \ 化合物	66	67	68	69	70	71	72	73	74	75	76	77	78	79
1											154.00	151.53	152.33	154.37
2	141.5	162.7	150.6	138.3	142.6	148.8	160.4	133.6	142.0	152.2	105.03	108.87	107.99	102.24
3	108.6	101.1	104.7	118.6	113.5	105.3	101.2	135.0	127.3	126.4	111.63	112.30	112.05	111.27
4		108.9	109.4	111.3				100.4	105.7	103.4	141.97	143.98	143.37	140.68
5		139.5	139.6	141.6				162.9	146.4	156.2				
CH_3			13.0	9.2	10.9									
					8.0									

① 化合物 66 ~ 72,74 ~ 75 在 CCl_4 中测定。

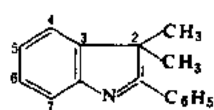
66. R = H
67. R = C(CH_3)$_3$
68. 2-CH_3
69. 3-CH_3
70
71. R = CH_3
72. R = C(CH_3)$_3$
73
74. R = CH_3
75. R = C(CH_3)$_3$
76. R = H
77. R = NO_2
78. R = CHO
79. R = NH_2

表 16-5 吲哚类化合物 80 ~ 93 的^{13}C-NMR 化学位移数据[39 ~ 42,44]

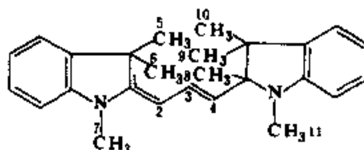
C \ 化合物	80	81	82	83①	84①	85	86	87	88①	89①	90	91	92	93
1											183.10		29.3	29.0
2	125.2	135.7	122.7	126.4	145.9	123.7	137.4	121.3	42.7	44.8	152.99	95.4	24.3	29.0
3	102.6	100.4	111.4	103.8	107.3	103.1	98.5	117.5	28.0	27.4	147.47	126.8	83.6	80.7
4	121.3	120.0	119.4	122.5	123.6	120.5	119.7	119.2	133.0	132.4	120.77	126.7		
5	120.3	119.9	119.6	123.5	125.1	121.8	121.2	121.8	125.4	126.3	125.72	28.3		
6	122.3	121.1	122.3	121.5	122.0	119.9	119.1	119.8	124.4	124.1	127.66	28.3		
7	111.8	110.9	111.7	113.0	112.1	110.0	110.9	111.1	127.5	127.8	120.77	29.5		
8				130.0	128.5	135.2	136.8		116.4	110.0		15.5		
9				137.3	155.9	128.8	128.2	125.1	142.2	142.0		25.2		
10									159.9	157.8		25.2		
11												28.8		
R														

① 化合物 83 ~ 84 在二氧六环中测定,88 ~ 89 在(CD_3)$_2$CO 中测定。

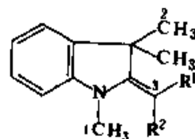
80. R = H
81. R = 2-CH_3
82. R = 3-CH_3
83. X = NH
84. X = O
85. 1-C_6H_5
86. 2-C_6H_5
87. 3-C_6H_5
88
89



90



91

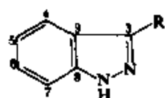


92. $R^1 = COOCH_3, R^2 = H$

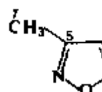
93. $R^1 = H, R^2 = COOCH_3$

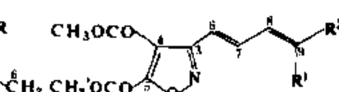
表 16-6　2 个杂原子的五元杂环化合物 94～107 的 ^{13}C-NMR 化学位移数据[45～51]

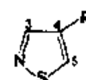
C \ 化合物	94	95	96	97	98	99	100	101	102	103	104	105	106	107
3	133.4	132.2	149.0	149.13	159.16	150.95	169.0	164.2	157.1	157.0	157.9	152.8	166.7	157.6
4	120.4	119.4	120.1	103.69	105.6	101.45	102.3	109.0	116.0	117.5	107.0	146.8	123.9	123.3
5	120.1	121.3	117.2	157.89	159.16	169.25	159.9	159.9	158.8	158.6	147.0	151.9	148.1	163.0
6	125.8	127.3	125.9				12.1	10.7	125.3	124.6				
7	110.0	110.9	109.2				13.3	10.0	132.6	134.1				
8	139.9	141.1	141.4						147.6	148.6				
9	122.8	118.5	113.9						102.5	104.0				
R								6.6	114.4	113.9			18.5	12.6

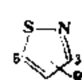












94. R = H
95. R = Cl
96. $R = NH_2$

97. R = N
98. $R = 3\text{-}CH_3$
99. $R = 5\text{-}CH_3$

100. R = H
101. $R = CH_3$

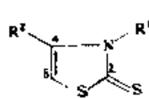
102. $R^1 = CN, R^2 = H$
103. $R^1 = H, R^2 = CN$

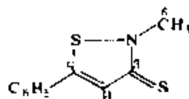
104. R = Br
105. $R = NO_2$

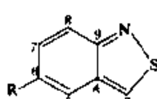
106. $R = 3\text{-}CH_3$
107. $R = 5\text{-}CH_3$

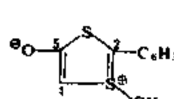
表 16-7　2,3 个杂原子的五元杂环化合物 108～121 的 ^{13}C-NMR 化学位移数据[51～55]

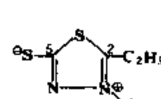
C \ 化合物	108	109	110	111	112	113	114	115	116	117	118	119	120	121
2	187.1	190.1					141.3	173.8						
3			186.7	187.3	144.5	150.9							152.2	113.8
4	132.6	144.8	125.3	134.4	134.5	138.0	108.1		134.0	133.3	96.77	94.23		156.1
5	110.9	109.0	155.4	151.7	122.1	120.0	172.8	183.2	121.7	136.3	169.2	169.7		
6			31.6	36.1	124.2	145.1			136.6	136.6			7.9	7.4
7					128.6	122.8			120.2	124.7				10.9
8					121.6	122.2			129.4	129.3				
9					161.5	161.9			128.4	129.3				

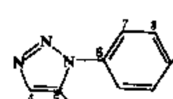












108. $R^1 = CH_3, R^2 = H$
109. $R^1 = R^2 = C_6H_5$

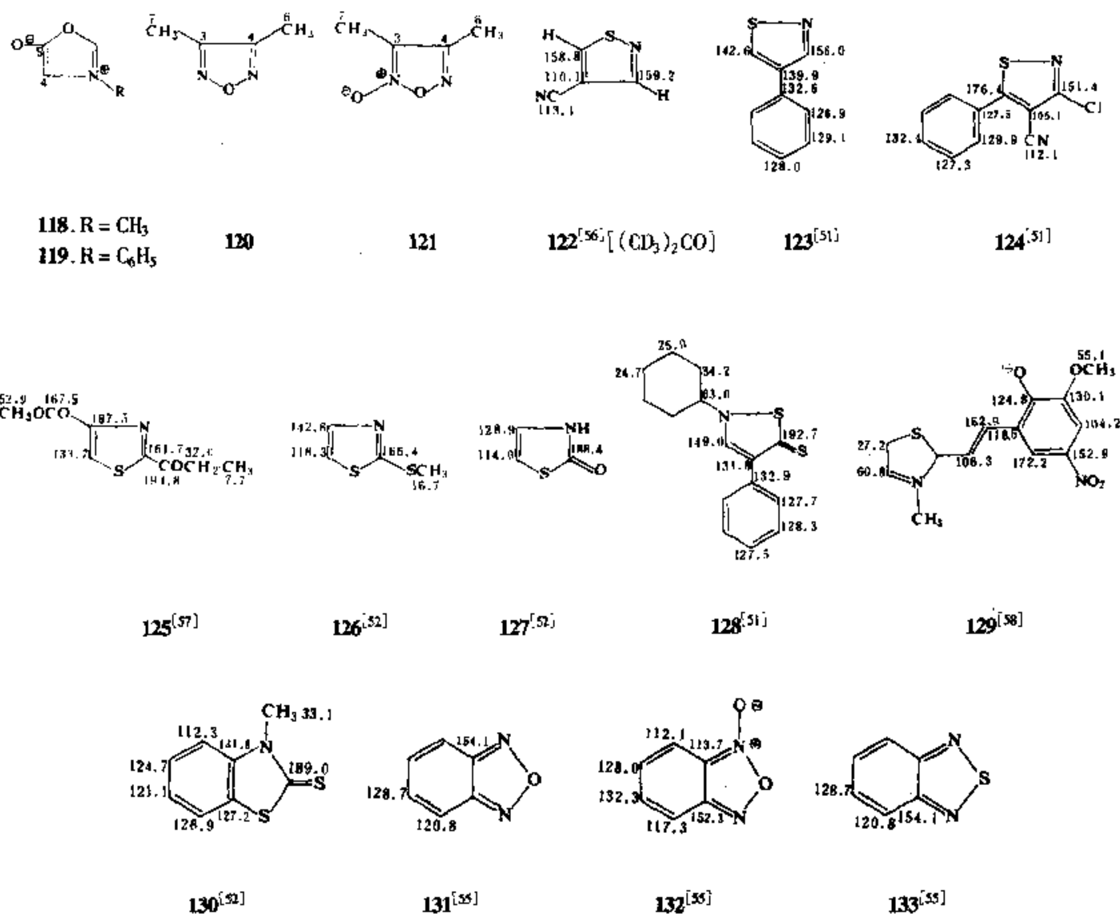
110. R = H
111. $R = C_6H_5$

112. R = H
113. $R = NO_2$

114

115

116. R = H
117. $R = CH_2NHCH(CH_3)_2$



第三节 六元及七元杂环化合物的^{13}C-NMR 化学位移

一、单取代吡啶的^{13}C-NMR 化学位移数据的加和值



$\delta_{C-2} = 149.8 + Z_{i2}$ $\delta_{C-5} = 123.6 + Z_{i5}$

$\delta_{C-3} = 123.6 + Z_{i3}$ $\delta_{C-6} = 149.8 + Z_{i6}$

$\delta_{C-4} = 135.7 + Z_{i4}$

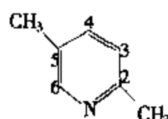
1或6取代(i为1或6)	$Z_{22} = Z_{66}$	$Z_{23} = Z_{65}$	$Z_{24} = Z_{64}$	$Z_{25} = Z_{63}$	$Z_{26} = Z_{62}$
—CH_3	8.8	−0.6	0.2	−3.0	−0.4
—CH_2CH_3	13.6	−1.8	0.4	−2.9	−0.7
—F	14.4	−13.1	6.1	−1.5	−1.5
—Cl	2.3	0.7	3.3	−1.2	0.6
—Br	−6.7	4.8	3.3	−0.5	1.4
—OH	15.5	−3.5	−0.9	−16.9	−8.2
—OCH_3	15.3	−7.5	2.1	−13.1	−2.2
—NH_2	11.3	−14.7	2.3	−10.6	−0.9
—NO_2	8.0	−5.1	5.5	6.6	0.4
—CHO	3.5	−2.6	1.3	4.1	0.7
—$COCH_3$	4.3	−2.8	0.7	3.0	−0.2
—CN	−15.9	5.0	1.6	3.6	1.4

续表

3或5-取代($i=3$或5)	$Z_{32}=Z_{56}$	$Z_{33}=Z_{55}$	$Z_{34}=Z_{54}$	$Z_{35}=Z_{53}$	$Z_{36}=Z_{52}$
$-CH_3$	1.3	9.0	0.2	-0.8	-2.3
$-CH_2CH_3$	-0.4	15.5	-0.6	-0.4	-2.7
—F	-11.5	36.2	-13.0	0.9	-3.9
—Cl	-0.3	8.2	-0.2	0.7	-1.4
—Br	2.1	-2.6	2.9	1.2	-0.9
—I	7.1	-28.4	9.1	2.4	0.3
—OH	-10.7	31.4	-12.2	1.3	-8.6
$-NH_2$	-11.9	21.5	-14.2	0.9	-10.8
—CHO	2.4	7.9	0.0	0.6	5.4
$-COCH_3$	3.5	8.6	-0.5	-0.1	0.0
$-CONH_2$	2.7	6.0	1.3	1.3	-1.5
—CN	3.6	-13.7	4.4	0.6	4.2

4-取代($i=4$)	$Z_{42}=Z_{46}$	$Z_{43}=Z_{45}$	Z_{44}
$-CH_3$	0.5	0.8	10.8
$-CH_2CH_3$	-0.1	-0.4	17.0
$-CH(CH_3)_2$	0.4	-1.8	21.4
$-C(CH_3)_3$	0.1	-3.4	23.4
$-CH=CH_2$	0.3	-2.9	8.6
—F	2.7	-11.8	33.0
—Br	3.0	3.4	-3.0
$-NH_2$	0.9	-13.8	19.6
—CHO	1.7	-0.6	5.5
$-COCH_3$	1.6	-2.6	6.8
—CN	2.1	2.2	-15.7

举例：



(C-2)	基本值	149.8
	$Z_{22}(CH_3)$	8.8
	$Z_{52}(CH_3)$	-2.3
	计算值	156.3
	实测值	155.2

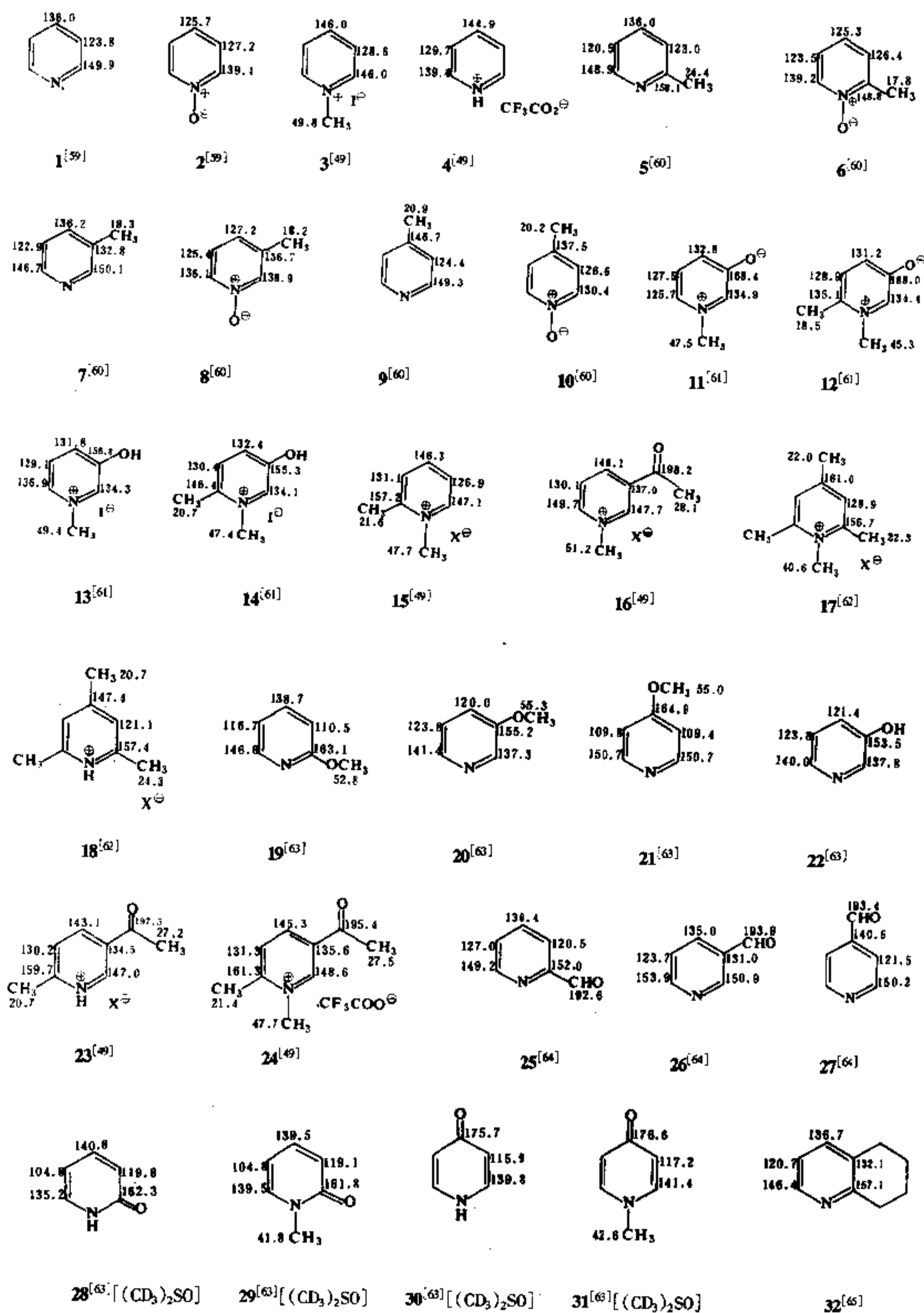
(C-3)	基本值	123.6
	$Z_{23}(CH_3)$	-0.6
	$Z_{53}(CH_3)$	-0.8
	计算值	122.2
	实测值	122.5

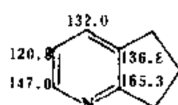
(C-4)	基本值	135.7
	$Z_{24}(CH_3)$	0.2
	$Z_{54}(CH_3)$	0.2
	计算值	136.1
	实测值	136.7

(C-5)	基本值	123.6
	$Z_{55}(CH_3)$	9.0
	$Z_{25}(CH_3)$	-3.0
	计算值	129.6
	实测值	129.6

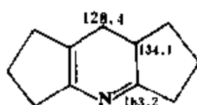
(C-6)	基本值	149.8
	$Z_{56}(CH_3)$	1.3
	$Z_{26}(CH_3)$	-0.4
	计算值	150.7
	实测值	149.4

二、吡啶类化合物的^{13}C-NMR化学位移

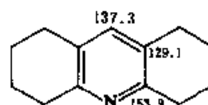




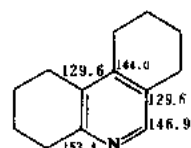
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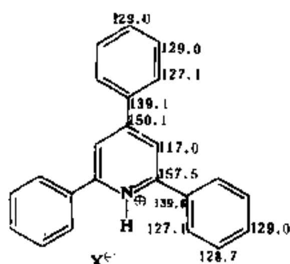
34[65]



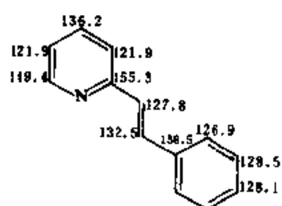
35[65]



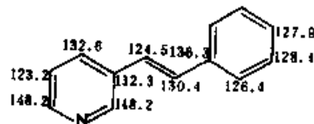
36[65]



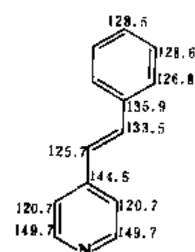
37[65][四氢呋喃 + CD_2Cl_2]



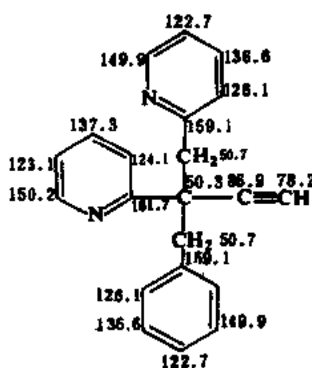
38[66]



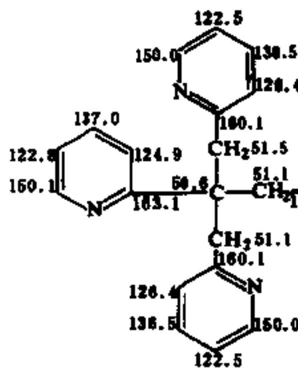
39[66]



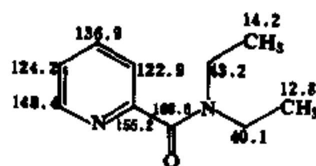
40[66]



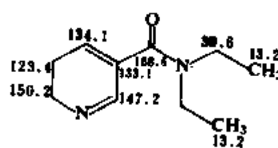
41[67]



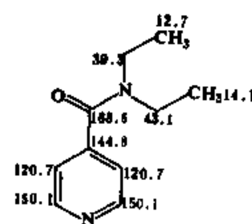
42[67]



43[68]

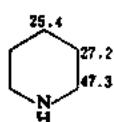


44[58]

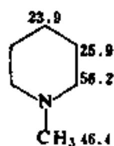


45[68]

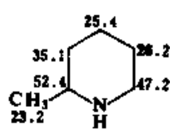
三、哌啶及其衍生物的^{13}C-NMR化学位移



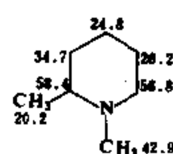
46[69]



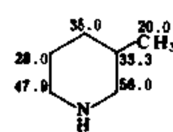
47[69]



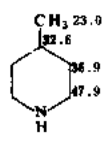
48[69]



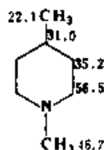
49[69]



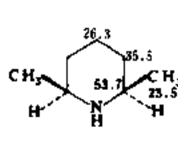
50[70][C_6D_6]



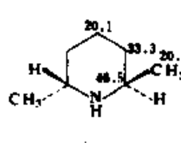
51[70] [C_6D_6]



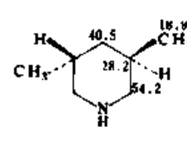
52[70] [C_6D_6]



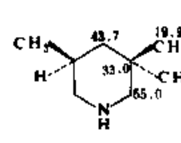
53[70] [C_6D_6]



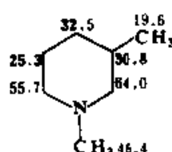
54[70] [C_6D_6]



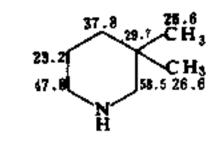
55[70] [C_6D_6]



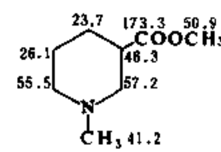
56[70] [C_6D_6]



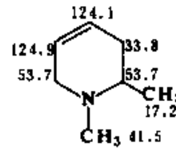
57[71]



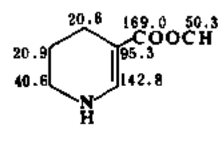
58[72]



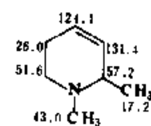
59[72]



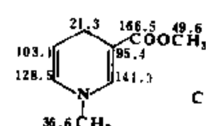
60[72]



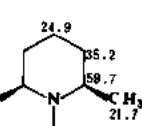
61[72]



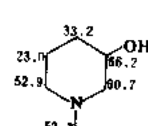
62[72]



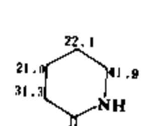
63[72]



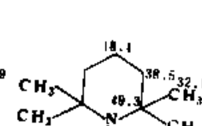
64[73]



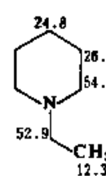
65[73]



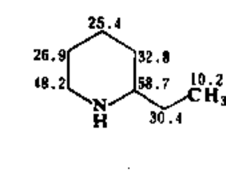
66[73]



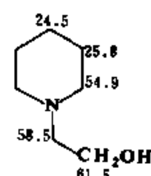
67[70]



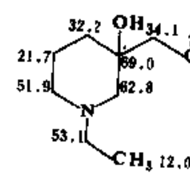
68[70]



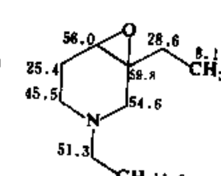
69[70]



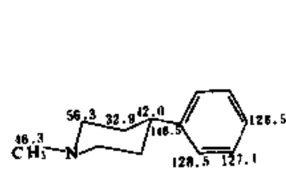
70[70]



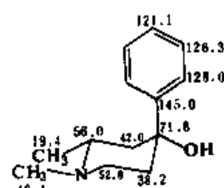
71[74]



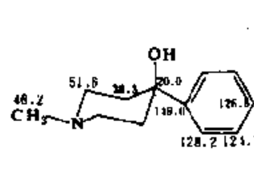
72[74]



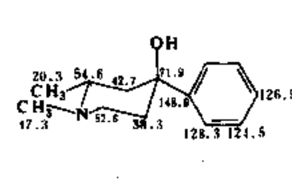
73[75]



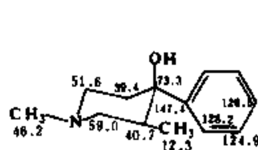
74[75]



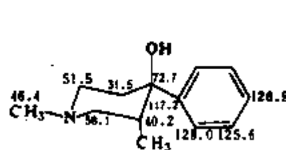
75[75]



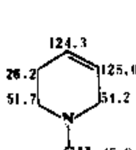
76[75]



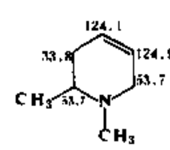
77[75]



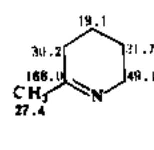
78[75]



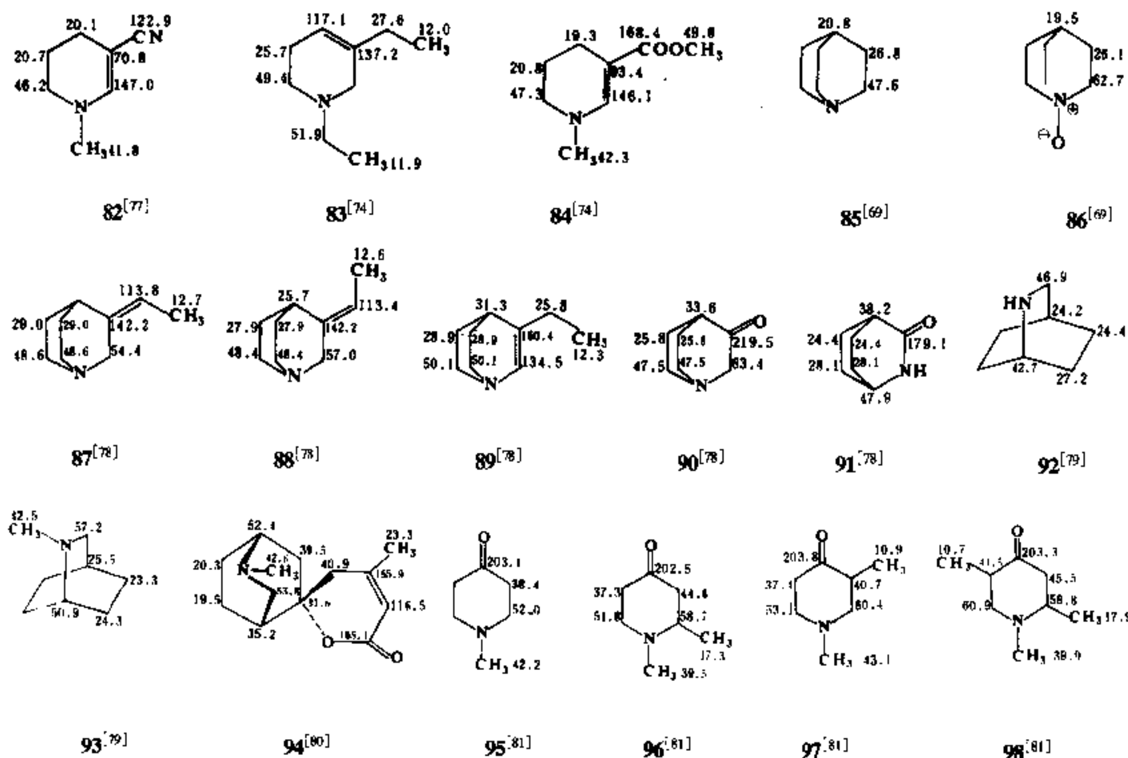
79[76]



80[76]



81[77]



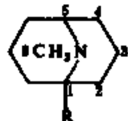
四、其他六元杂环化合物的^{13}C-NMR化学位移

表 16-8 并环杂环化合物 99 ~ 112 的^{13}C-NMR化学位移数据[82~86]

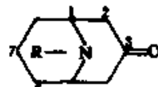
C \ 化合物	99	100	101	102	103	104	105	106	107	108	109	110	111	112
1	46.6	55.2	52.3	82.5	55.8	53.6	50.6	48.4	47.2	82.7	62.2	127.9	128.8	127.8
2			26.4	33.8	41.8	42.4	42.7	47.0				119.6	122.9	126.5
3	46.6	57.7	20.4	22.0	210.0	210.1	211.3	212.7	47.2	51.7	49.3	126.4	127.5	126.5
4	30.6	32.3	26.4	25.6					37.6	35.4	26.0	113.0	116.4	126.7
5	133.1	134.3	52.3	57.6					27.5	31.1	29.0	140.5	152.0	133.8
6	134.8	132.9			29.7	30.0	30.3	32.3	37.0	34.9	35.6	29.1	27.9	39.1
7	27.1	28.1			16	16.8	16.6	17.2				119.2	120.5	136.1
8	23.9	22.8												
9		46.2	40.9	34.2										



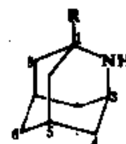
99. R = H
100. R = CH_3



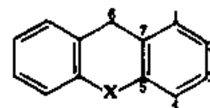
101. R = H
102. R = OH



103. R = CH_3
104. R = C_2H_5
105. R = $CH(CH_3)_2$
106. R = $C(CH_3)_3$



107. R = H
108. R = Cl
109. R = NH_2



110. X = NH
111. X = O
112. X = S

表 16-9 2 个氮原子的六元杂环化合物 113～126 的^{13}C-NMR 化学位移数据[87～92]①

C \ 化合物	113	114	115	116	117	118	119	120	121	122	123	124	125	126
2	153.4	145.5	166.4	154.6	150.1	158.39	163.42	159.1	161.6	161.7	157.9	157.1		
3				145.4	145.7						157.7	147.0	154.16	153.52
4	160.5	159.6	160.0			156.90	157.85	161.4	161.2	161.4			128.91	127.73
5	121.5	125.2	115.8	142.6	143.0	121.86	110.04	122.3	108.3	109.6	124.0	134.1	133.87	133.45
6				144.6	144.7	156.90	157.85	158.3	158.8	158.9	123.5	123.3	160.42	159.02
R		116.6	54.8	24.0							29.2	19.3		

① 化合物 113～115 在$(CD_3)_2CO$中测定，化合物 125～126 在重氢二甲基甲酰胺中测定。

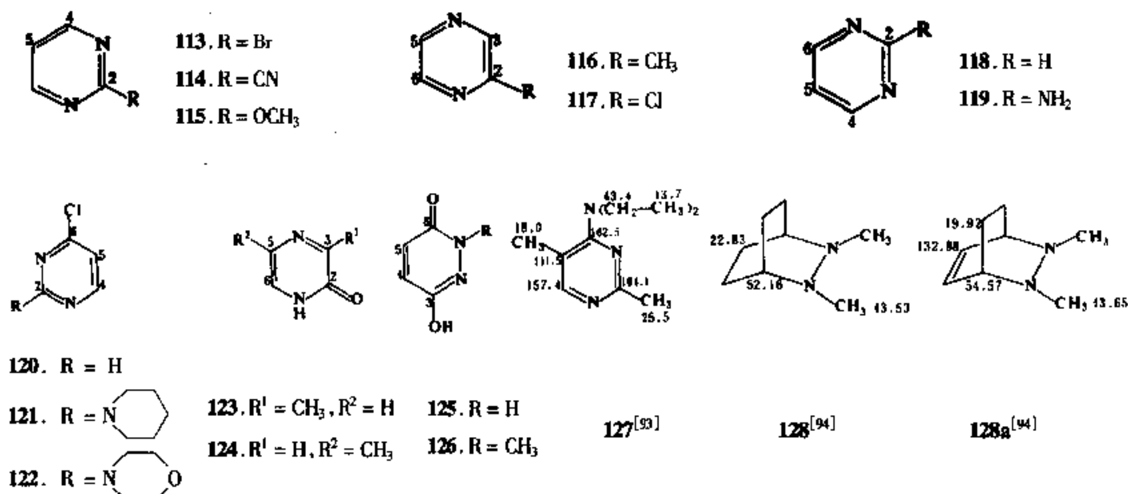


表 16-10 2 个杂原子的六元杂环化合物 129～142 的^{13}C-NMR 化学位移数据[95～100]

C \ 化合物	129	130	131	132①	133①	134①	135①	136	137	138	139	140	141	142
1						151.7	145.8	142.7	148.2	135.0	150.81	144.59	163.1	143.4
2	151.45	150.69	150.07	161.1	165.0	97.8	100.1	125.9	126.8	128.1	62.59	54.73	31.4	126.9
3						30.6	24.8	128.5	124.2	113.8	28.01	32.87	22.4	24.2
4	164.26	160.81	159.75	173.6	173.9	22.8	23.3	128.9	147.7	160.3	34.59	17.01	22.0	20.2
5	100.28	135.90	106.02			31.6	23.7				104.22	24.33	28.3	25.3
6	142.13	122.61	139.60	144.2	139.1	49.3	27.2					105.20	124.3	140.6
7				150.2	149.1	66.6	48.9	201.1	197.7	201.2	48.33		96.4	70.7
8							67.0	49.6	49.4	50.2	66.33	48.27	118.2	119.2
9				155.0	157.2			66.7	66.6	66.6		66.72	165.2	167.6
10				132.8	130.7									
11								66.7	66.6	66.6				
12								52.6	52.7	52.6				

① 化合物 132～133 在 3N NaOH 中测定，134～135 在 C_2Cl_4 中测定。

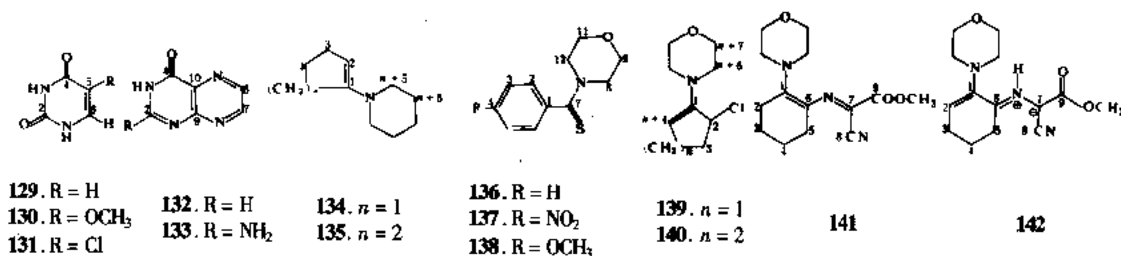
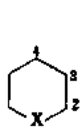


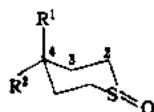
表 16-11　六元杂环化合物 143～156 的^{13}C-NMR 化学位移数据[24,101～105]

C \ 化合物	143	144	145	146	147	148	149	150	151①	152①	153	154	155	156
1					33.2	37.3	33.6	54.2			75.6	82.6		
2	29.1	45.8	45.74	50.66	32.1	62.4	130.3	121.8	153.2	154.1	47.2	48.3	141.0	118.3
3	27.9	26.1	23.73	29.95	21.6	32.5	129.0	129.8					147.7	152.5
4	26.6	24.5	30.89	30.45	32.1	28.3	35.3	32.6	42.5	45.0	60.0	59.4		
5							32.8	52.5	21.5	22.1			143.1	142.3
6							30.6	28.2	42.5	48.7			142.9	145.2
7							18.0	14.7	12.0	12.7				
R			22.43	20.72						37.6				

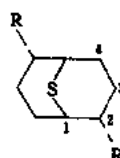
① 化合物 151～152 在$(CD_3)_2SO$中测定。



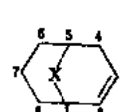
143. X = S
144. X = $NCOC_6H_5$



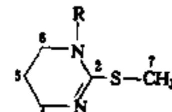
145. $R^1 = CH_3, R^2 = H$
146. $R^1 = H, R^2 = CH_3$



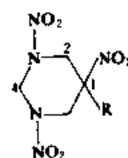
147. R = H
148. R = Cl



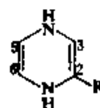
149. X = S
150. X = SO_2



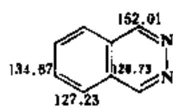
151. R = H
152. R = CH_3



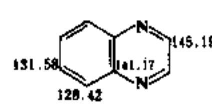
153. R = H
154. R = $CHONO_2$



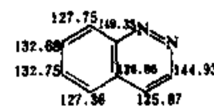
155. R = Br
156. R = I



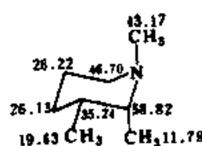
157[106] [D_2O]



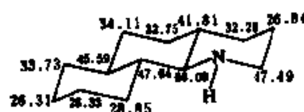
158[106]



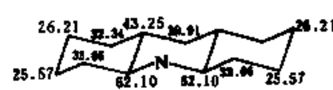
159[106]



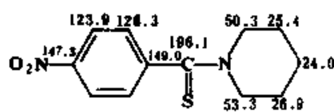
160[107]
[C_2HCl_3-$(CD_3)_2CO$]



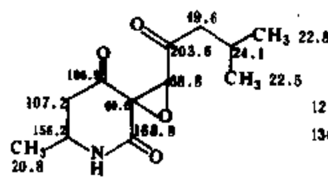
161[108]



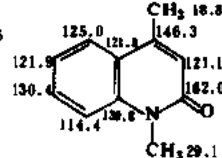
162[108]



163[96]



164[109]



165[110]

166[38] 167[111] 168[96] [CF_3COOH] 169[97]

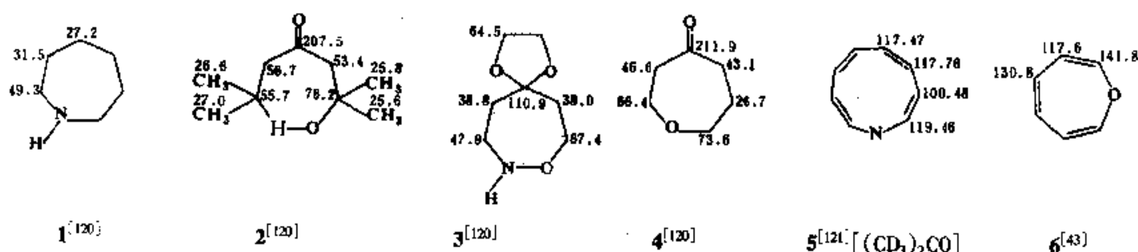
170[112] 171[112] 172[113] [$(CH_3)_2SO$] 173[113] [$(CH_3)_2SO$] 174[114]

175[115] 176[116] 177[116] 178[116] 179[116]

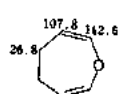
180[116] 181[116] 182[116] 183[117] 184[117] 185[116]

186[118] 187[118] 188[119] [CF_2Cl_2] 189[119] [CF_2Cl_2] 190[110] [CF_2Cl_2]

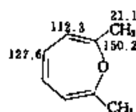
五、七元杂环化合物的^{13}C-NMR 化学位移



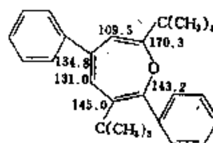
1[120] 2[120] 3[120] 4[120] 5[121] [$(CD_3)_2CO$] 6[43]



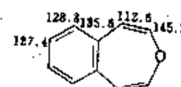
7[43]



8[43]



9[6][CS_2]



10[6][CS_2]

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115 Katrizkyyy A R et al. Tetrahedron Lett, 1977; 3803
116 Braun S et al. Org Magn Reson, 1975; 7: 194
117 Braun S et al. Org Magn Reson, 1975; 7: 199
118 Radel R J et al. J Org Chem, 1977; 42: 546
119 Baker V J et al. J Am Chem Soc, 1976; 98: 5748
120 Rice K C et al. Org Magn Reson, 1976; 8: 449
121 Anastassion A G et al. J Am Chem Soc, 1976; 98: 8266

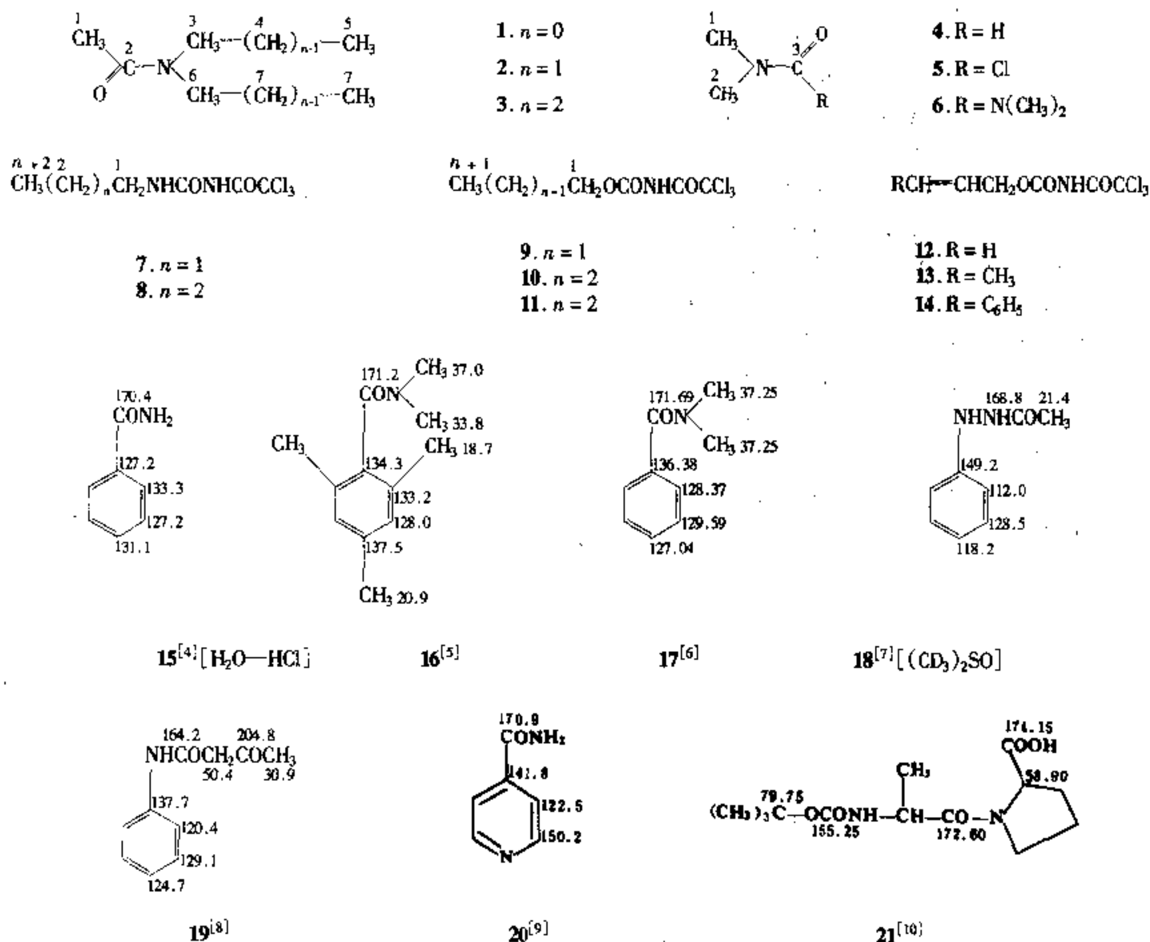
第十七章　有机含氮化合物的^{13}C-NMR 化学位移

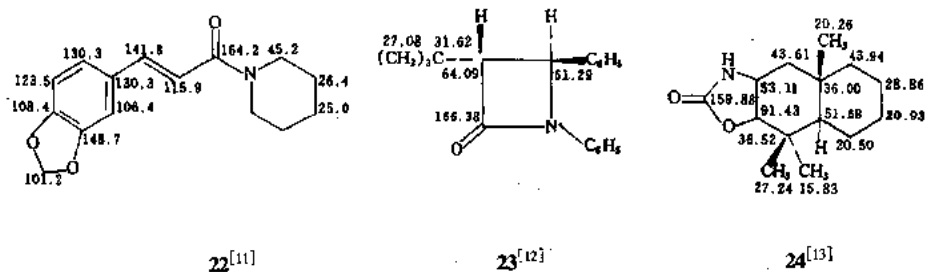
第一节　酰胺和脲类化合物的^{13}C-NMR 化学位移

表 17-1　酰胺类化合物 1～14 的^{13}C-NMR 化学位移数据[1～3]

C \ 化合物	1①	2①	3①	4	5	6	7	8	9	10	11	12	13	14
1	169.29	168.55	169.00	31.1	38.3	38.6	42.08	40.03	63.35	68.64	67.11	67.65	67.76	67.87
2	21.32	21.22	21.39	36.2	40.2	38.6	22.66	31.40	14.14	22.13	30.54	130.80	123.98	121.39
3	37.11	42.55	50.28	162.4	149.3	165.7	11.53	19.96		10.46	18.88	119:88	133.26	135.73
4		14.20	22.36					13.70			13.59		17.80	
5			11.13											
6	34.58	39.96	47.44											
7		13.37	21.39											
8			11.57											

① 化合物 1～3 在 C_6D_6 中测定。



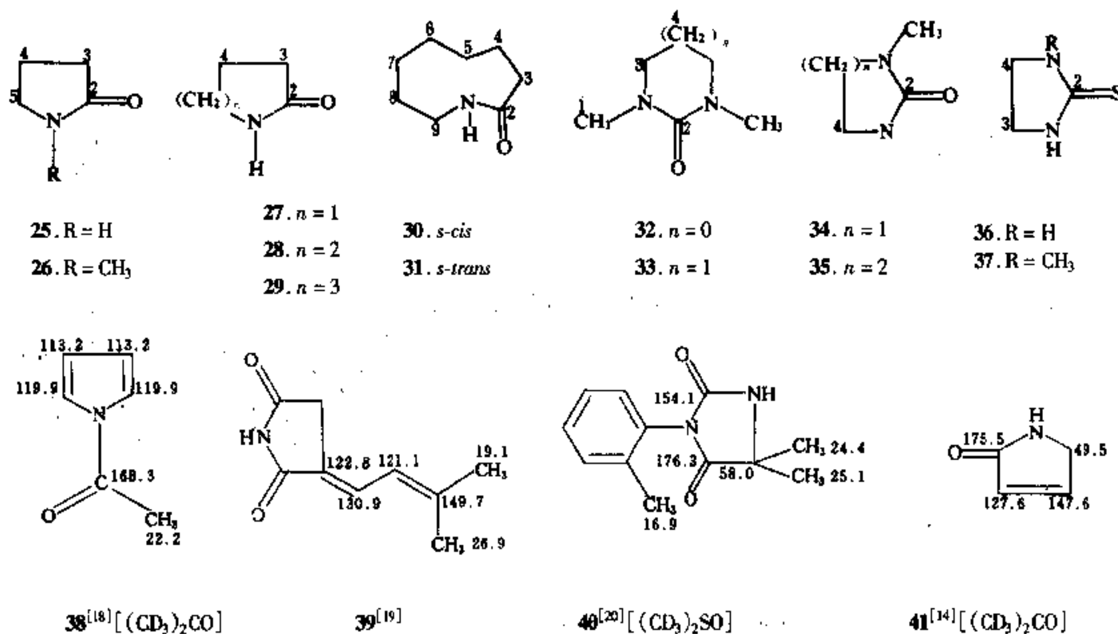


22[11]　　23[12]　　24[13]

表 17-2　内酰胺及脲类化合物 25～37 的^{13}C-NMR 化学位移数据[1,14,15,17]

C \ 化合物①	25	26	27	28	29	30	31	32	33	34	35	36	37
1								31.3	35.6				
2	179.4	174.3	179.8	173.1	179.9	177.5	175.9	161.3	156.7	162.9	156.7	183.8	183.2
3	30.6	30.8	30.4	31.5	36.9	33.2	37.4	45.0	48.1			44.4	40.7
4	21.3	18.2	20.8	20.9	23.4	22.4	23.2		22.5	37.3	40.1	44.4	50.4
5	42.7	49.4	20.8	22.3	30.7	29.1	28.6			47.0	22.3		
6				22.3	30.7	27.1	28.2				47.4		
7				42.0	42.7	24.5	25.3						
8						24.7	24.3						
9						39.3	39.3						
R		29.3											

① 化合物 34～37 在[$(CD_3)_2SO$]中测定。



25. R = H　26. R = CH_3

27. n = 1　28. n = 2　29. n = 3

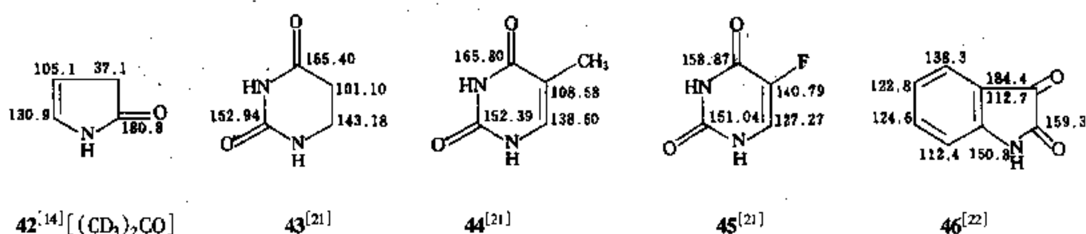
30. *s-cis*　31. *s-trans*

32. n = 0　33. n = 1

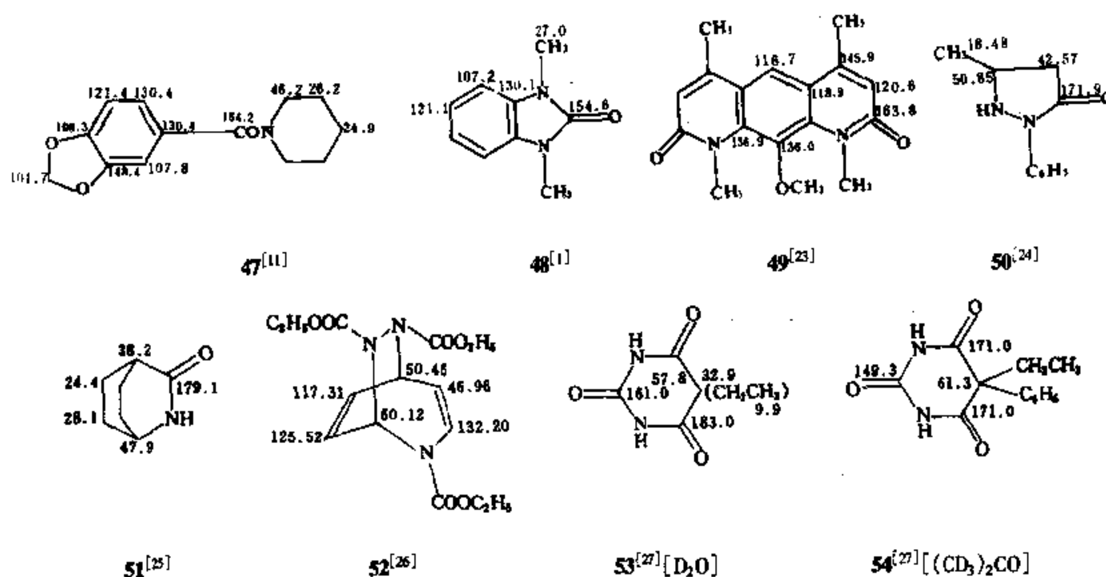
34. n = 1　35. n = 2

36. R = H　37. R = CH_3

38[18][$(CD_3)_2CO$]　　39[19]　　40[20][$(CD_3)_2SO$]　　41[14][$(CD_3)_2CO$]



42[14][$(CD_3)_2CO$]　　43[21]　　44[21]　　45[21]　　46[22]



第二节 腈、异腈及其衍生物的^{13}C-NMR 化学位移

一、腈及其衍生物的^{13}C-NMR 化学位移

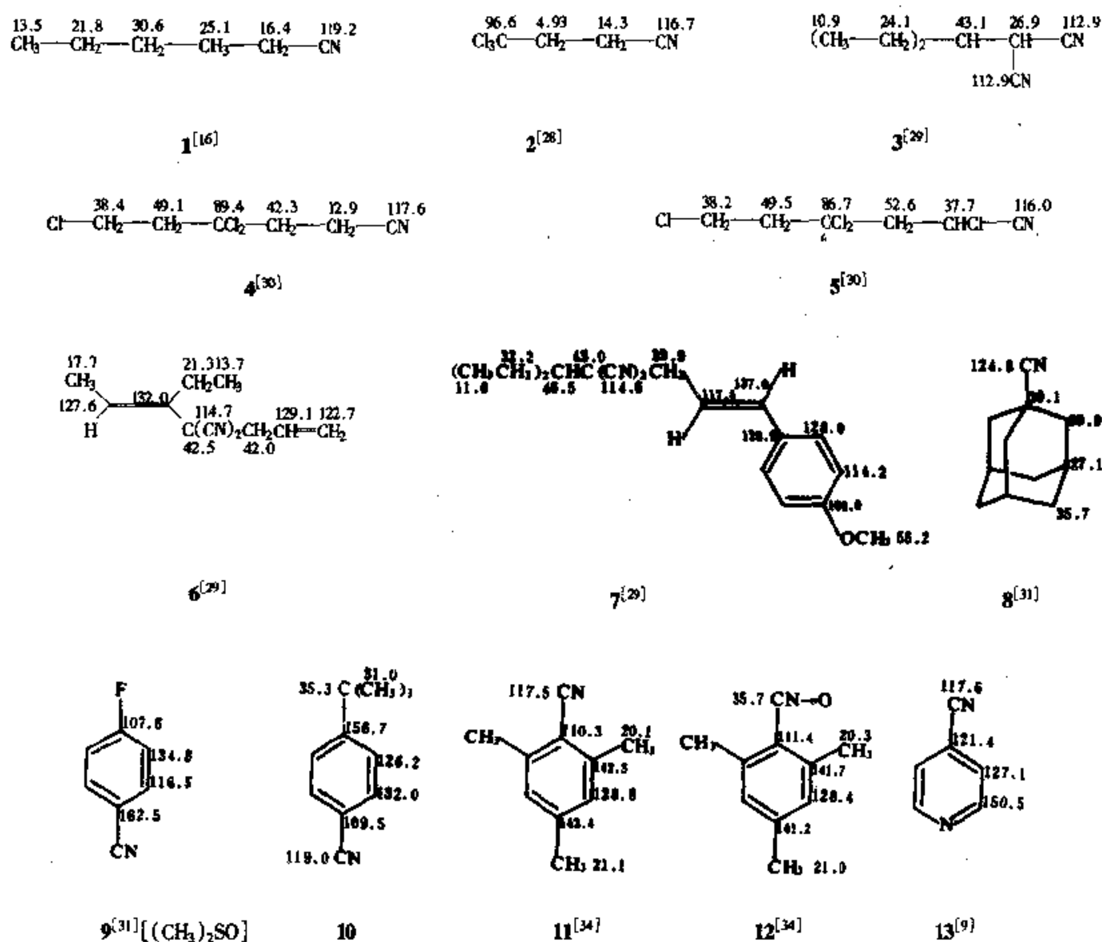
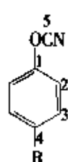
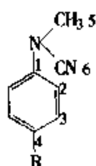


表 17-3 氰酸酯和氰胺类化合物 14~19 的^{13}C-NMR 化学位移数据[35]

化合物 / C	14	15	16	17	18	19	化合物 / C	14	15	16	17	18	19
1	153.5	147.5	156.9	141.4	134.7	140.4	5	109.2	109.9	107.9	114.5	115.2	111.4
2	115.8	116.8	117.1	115.3	115.4	117.4	6				37.3	37.6	37.8
3	131.2	116.0	126.9	130.3	116.8	130.3	R		56.4			56.2	
4	127.5	158.8	146.5	123.7	156.6	128.9							

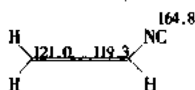


14. R = H
15. R = OCH_3
16. R = NO_2

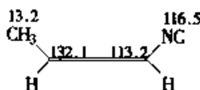


17. R = H
18. R = OCH_3
19. R = Cl

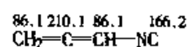
二、异腈化合物的^{13}C-NMR 化学位移



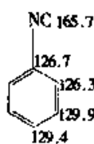
20[36]



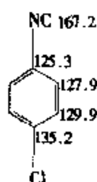
21[36]



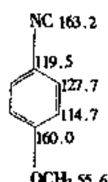
22[37] [CCl_4/CD_3CN]



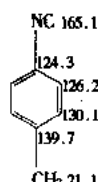
23[37] [CCl_4/CD_3CN]



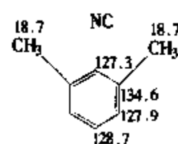
24[37] [CCl_4/CD_3CN]



25[36]

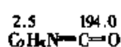


26[37] [CCl_4/CD_3CN]

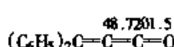


27[37] [CCl_4/CD_3CN]

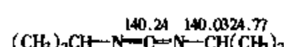
三、杂叠烯类化合物的^{13}C-NMR 化学位移



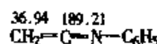
28[1]



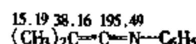
29[38]



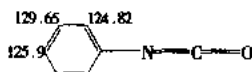
30[39]



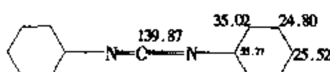
31[40]



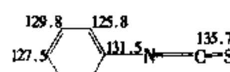
32[40]



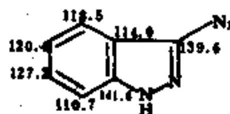
33[41]



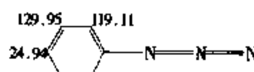
34[39]



35[1]



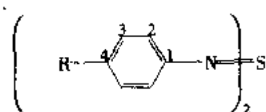
36[42] [$(CD_3)_2SO$]



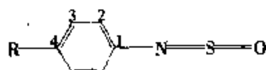
37[41]

表 17-4　化合物 38～48 的^{13}C-NMR 化学位移数据[43]

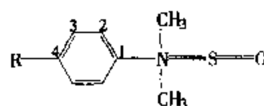
C \ 化合物	38	39	40	41	42	43	44	45	46	47	48
1	145.5	140.1	143.7	144.0	142.7	137.4	141.2	146.9	145.4	144.2	151.0
2	123.2	124.8	123.2	124.5	127.1	129.5	128.4	127.9	123.2	124.3	122.2
3	128.8	114.1	129.3	129.0	129.1	114.2	129.5	125.5	129.1	128.9	131.0
4	126.6	158.4	136.6	132.5	130.4	161.0	136.2	148.0	121.8	126.5	123.0
R		55.1	21.1			55.4					CO 166.9 CH_3 51.7



38. R = H
39. R = OCH_3
40. R = CH_3
41. R = Cl

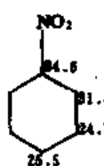


42. R = H
43. R = OCH_3
44. R = Cl
45. R = NO_2

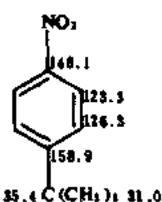


46. R = H
47. R = Cl
48. R = $COOCH_3$

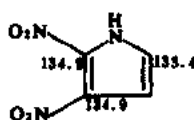
第三节　硝基和亚硝基类化合物的^{13}C-NMR 化学位移



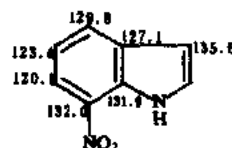
1[44]



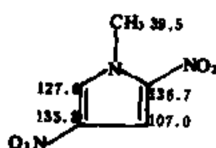
2[33]



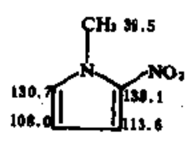
3[45]



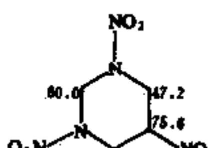
4[46][$(CD_3)_2SO$]



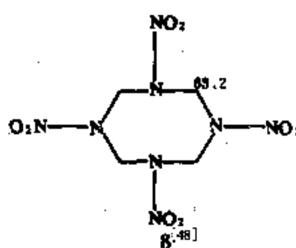
5[45][$(CD_3)_2CO$]



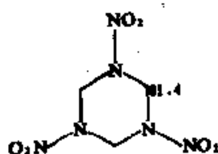
6[45][$(CD_3)_2CO$]



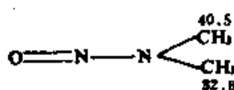
7[47]



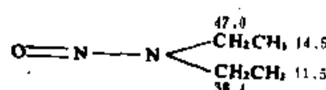
8[48]



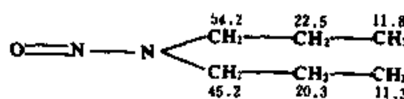
9[48]



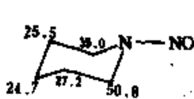
10[49]



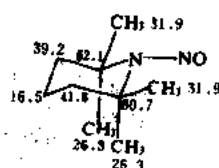
11[49]



12[49]



13[50]

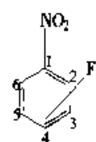


14[51]

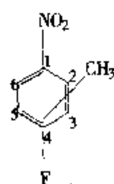
表 17-5 硝基化合物 15～27 的^{13}C-NMR 化学位移数据[32,52]

C \ 化合物①	15	16	17	18	19	20	21	22	23	24	25	26	27
1	134.8	146.8	143.4	144.9	141.3	145.5	131.2	132.6	126.4	153.0	163.8	149.7	162.0
2	153.6	111.2	126.2	136.5	124.8	107.9	158.6	114.9	132.4	139.9	113.6	140.8	116.0
3	118.2	163.2	116.4	118.6	124.8	136.6	121.5	161.8	120.5	125.8	125.1	124.9	125.1
4	136.0	122.4	164.5	164.0	161.3	145.5	134.4	119.1	163.8	120.9	141.0	123.9	141.8
5	125.8	131.9	116.4	113.5	114.7	117.9	119.5	126.2	112.0	134.5	125.1	133.4	
6	125.1	119.7	126.2	127.0	121.5	120.0	146.8	143.2	150.2	114.3	113.6	120.1	
1′												154.9	153.7
2′												118.6	119.9
3′												129.3	129.5
4′												122.7	124.7
OCH_3										57.4	55.9		

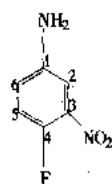
① 化合物 15～23 在$(CD_3)_2SO$ 中测定。



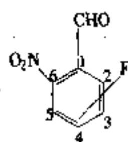
15. 2-F
16. 3-F
17. 4-F



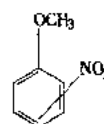
18. 2-CH_3
19. 3-CH_3



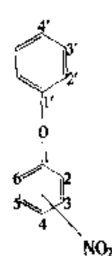
20



21. 2-F
22. 3-F
23. 4-F



24. 2-NO_2
25. 4-NO_2



26. 2-NO_2
27. 4-NO_2

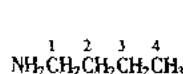
第四节 胺、亚胺及羟胺类化合物的^{13}C-NMR 化学位移

一、胺类化合物的^{13}C-NMR 化学位移

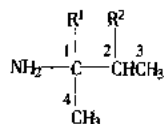
表 17-6 胺基化合物 1～14 的^{13}C-NMR 化学位移数据[53～55]①

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	42.06	50.02	55.79	53.81	57.40	15.72	10.29	36.50	36.86	47.56	12.60	14.24	40.07	50.9
2	36.18	27.95	33.37	31.80	33.21	44.43	29.63	54.16	55.11		46.92	20.96	36.66	37.0
3	21.06	9.95	8.17	18.65	25.75		55.64	61.14	41.94			30.28		26.3
4	14.75	18.15	24.98	15.37	14.50							54.28		26.9
R				17.50										

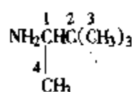
① 化合物 1～5,8～9,13～14 均在 D_2O 中测定。



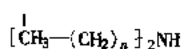
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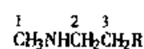
2. $R^1 = R^2 = H$
3. $R^1 = CH_3, R^2 = H$
4. $R^1 = H, R^2 = CH_3$



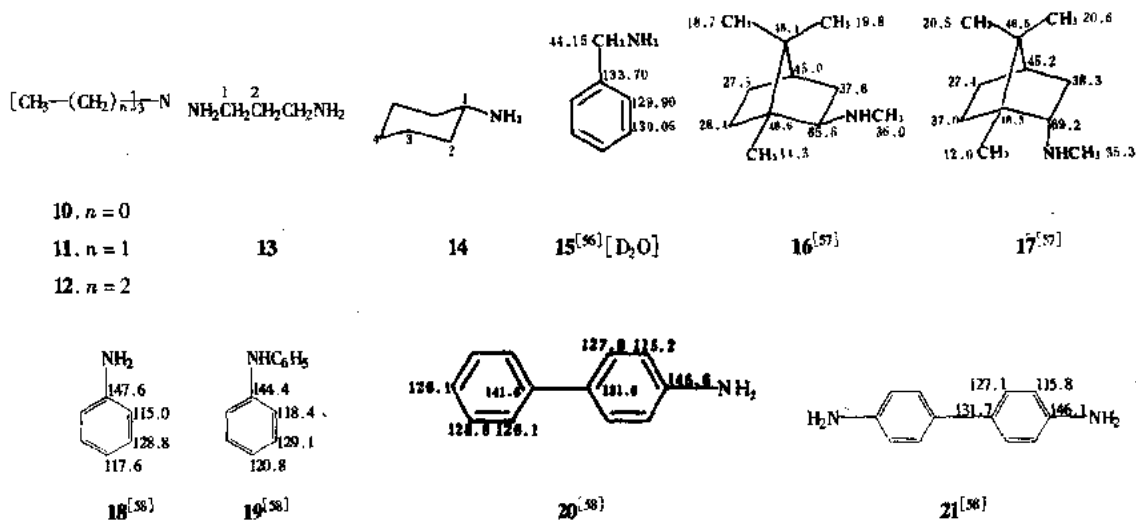
5



6. $n = 1$
7. $n = 2$



8. R = OH
9. R = NH_2



二、亚胺类化合物的^{13}C-NMR化学位移

表 17-7 亚胺类化合物 22 ~ 33 的^{13}C-NMR化学位移数据[59,60]

C \ 化合物	22	23	24	25	26	27	28	29	30	31	32	33
1	19.9	24.4	7.8	10.7	147.4	151.5	143.0	148.9	153.0	135.2	24.5	24.5
2	40.7	48.3	35.4	36.9	120.9	121.8	142.0	115.8	34.1	126.6	77.6	77.6
3	204.5	233.3	175.0	172.5	128.5	132.6	123.6	148.2	39.8	127.8	152.2	152.2
4	93.3	110.8	10.7	16.5	123.7	107.2	124.0	118.3		128.4	124.6	124.1
5	153.5	156.9	38.3	35.5	154.6	155.8	133.0	129.2		140.3	130.8	129.6
6	37.3	38.7			53.1	53.8	122.6	127.2		127.1	45.3	44.8
7	45.6	46.3					155.0	155.8		163.1	24.5	24.5
8							63.0	62.7		47.8		
9							14.1	14.1				
R											17.9	14.8

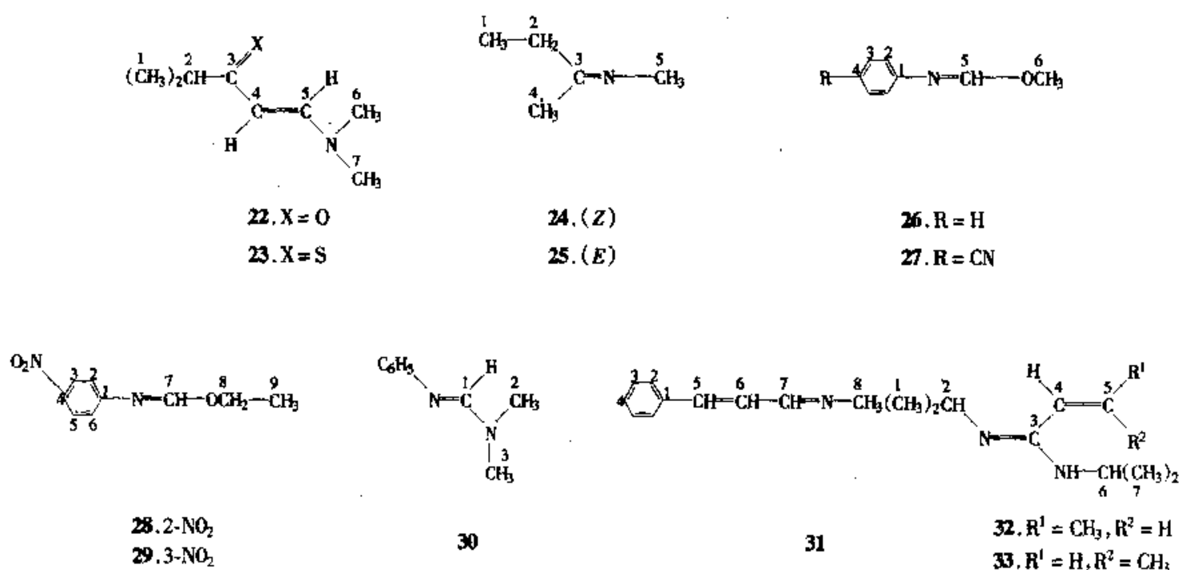
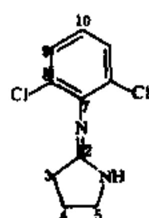


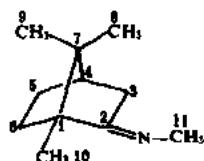
表 17-8　亚胺类化合物 34～45 的^{13}C-NMR 化学位移数据[22,57,61～64,1]①

化合物 / C	34	35	36	37	38	39	40	41	42	43	44	45
1			53.6			134.3	167.8	167.8	152.0	149.3	36.0	150.8
2	168.5	163.4	183.5		130.8	130.7	131.2	129.2	121.5	121.5	49.2	122.3
3	28.7	30.7	35.2	121.4	128.3	129.0	134.1	143.9	128.4	129.2		128.2
4	21.6	21.6	43.9	135.7	135.0	129.0	151.7	151.7	119.6	128.6		119.6
5	44.5	44.5	27.5	137.5	128.3	130.8					157.8	
6			32.1	139.7	130.3						34.8	
7	145.9	144.6	47.1	139.8					159.0	159.2		154.8
8	128.6	127.7	19.6	130.8					39.4	39.5		48.4
9	127.9	127.9	19.1	198.1								
10	122.7	122.7	11.3	27.7								35.0
11			39.3									
R										20.7		

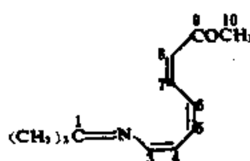
① 化合物 34～35 在 -60℃下测定；化合物 36 在 $CDCl_3/CF_3COOH$ 中测定；化合物 40～41 在$(CD_3)_2CO$ 中测定。



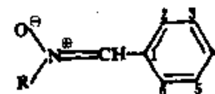
34.(*Z*)
35.(*E*)



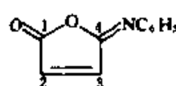
36



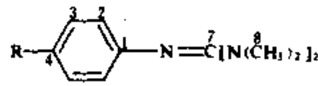
37



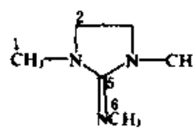
38. R = CH_3
39. R = C_6H_5



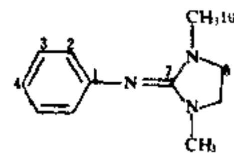
40.(*E*)
41.(*Z*)



42. R = H
43. R = CH_3



44

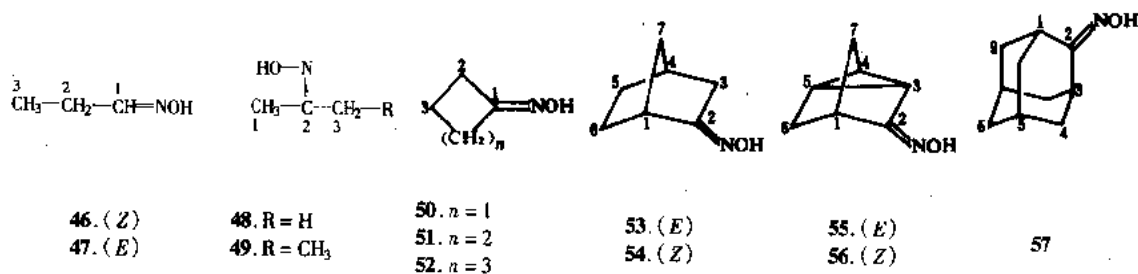


45

三、羟胺类化合物的^{13}C-NMR 化学位移

表 17-9　羟胺类化合物 46～57 的^{13}C-NMR 化学位移数据[65]

化合物 / C	46	47	48	49	50	51	52	53	54	55	56	57
1	153.7	153.1	15.0	13.0	159.7	167.1	160.4	42.0	38.5	29.0	33.4	29.1
2	18.6	23.1	155.4	159.1	30.7	27.1	25.7	167.4	166.3	167.6	167.1	167.4
3	10.4	10.9	21.7	28.9	14.6	25.1	25.4	34.9	37.2	13.8	11.4	36.2
4					31.6	24.4	24.4	35.5	35.6	16.7	17.1	37.7
5						30.6	26.7	27.1	26.0	33.3	33.6	27.9
6							31.9	27.8	27.4			36.6
7								39.1	38.3			
9												39.0
R				10.7								



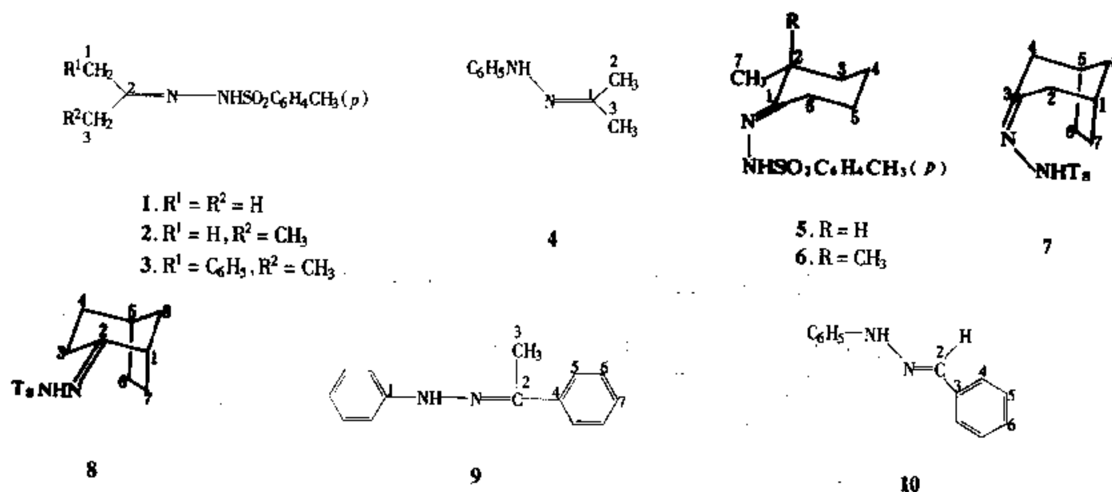
第五节 腙类、重氮及偶氮化合物的^{13}C-NMR 化学位移

一、腙类化合物的^{13}C-NMR 化学位移

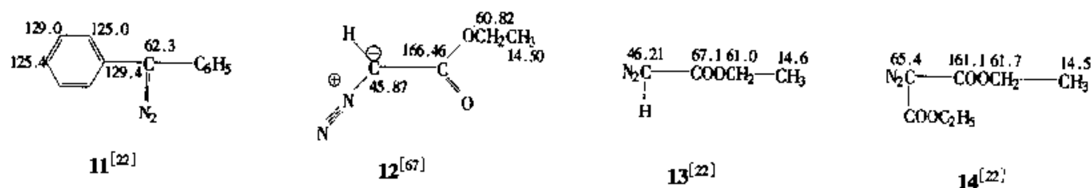
表 17-10 腙类化合物 1~10 的^{13}C-NMR 化学位移数据[60,66]

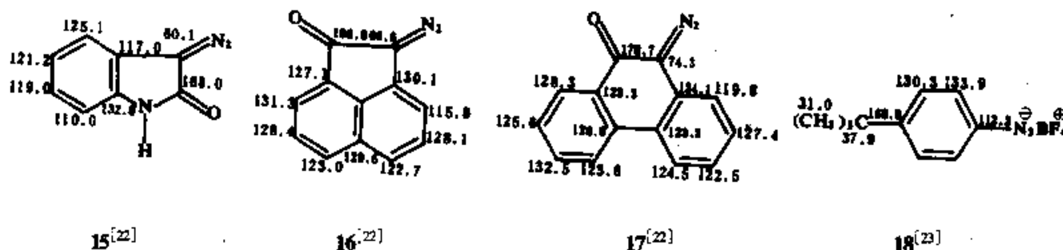
C \ 化合物	1	2	3	4	5	6	7	8	9①	10①
1	25.2	22.5	42.9	145.7	164.7	166.8	34.4	44.6	140.7	
2	149.8	160.7	161.2	15.1	39.2	39.2	35.2	167.1	146.2	145.8
3	17.2	23.6	22.0	24.8	35.5	40.9	160.4	29.5	12.5	137.0
4					24.5	21.4	42.6	31.3	139.8	126.1
5					26.2	26.2	34.9	34.1	125.5	128.7
6					26.5	23.3	29.4	28.2	128.2	128.0
7					16.9	26.9	28.3	27.6	127.4	
8							38.1	38.2		
R		9.5	9.5			26.9				

① 化合物 9~10 在$(CD_3)_2CO$中测定。



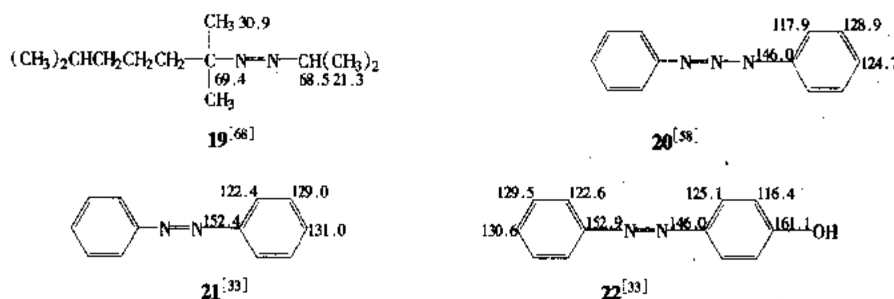
二、重氮化合物的^{13}C-NMR 化学位移





15[22]　16[22]　17[22]　18[23]

三、偶氮化合物的^{13}C-NMR 化学位移



19[68]　20[58]　21[33]　22[33]

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第十八章　含卤素、硫和磷化合物的^{13}C-NMR化学位移

第一节　卤代化合物的^{13}C-NMR化学位移

一、脂肪卤族化合物的^{13}C-NMR化学位移

表 18-1　脂肪卤族化合物 1～12 的^{13}C-NMR化学位移数据[1,2]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
1	95.3	101.2	99.6	96.3	98.2	109.1	36.7	54.0	77.5	46.7	42.2	40.1
2	45.5	49.0	56.8	56.8	73.4	81.1	91.1	87.7	89.4	26.5	35.6	45.3
3		10.8	19.6	38.5	45.3	24.1	42.7	46.2	54.1	11.5	42.2	70.1
4			12.5				9.8	38.6	67.4			

$\overset{1}{C}Cl_3\overset{2}{C}H_2(CH_2)_{n-2}\overset{n+1}{C}H_3$　　$\overset{1}{C}Cl\overset{2}{C}HR\overset{3}{C}H_2Cl$　　$Cl_3\overset{1}{C}\overset{2}{C}(\overset{3}{C}H_3)_2OH$　　$R^1(R^2)>\overset{1}{C}H\overset{2}{C}Cl_2\overset{3}{C}H_2\overset{4}{C}H<R^1(R^2)$　　$R^1(R^2)>\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2Cl$

1. $n=1$　　4. R = H　　6　　7. $R^1=R^2=H$　　10. $R^1=R^2=H$

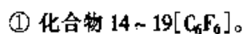
2. $n=2$　　5. R = Cl　　　　8. R = Cl, R^2 = H　　11. R^1 = Cl, R^2 = H

3. $n=3$　　　　　　9. $R^1=R^2=Cl$　　12. $R^1=R^2=Cl$

表 18-2　脂肪卤族化合物 13～23 的^{13}C-NMR化学位移数据[1,3-6]①

C \ 化合物	13	14	15	16	17	18	19	20	21	22	23
1	22.25	93.6	93.9	94.0	118.5	118.5	118.5	115.6	113.8	92.8	122.48
2	40.38	109.5	109.9	109.9	109.8	109.9	109.9	141.2	141.6	127.1	130.43
3	110.30	108.9	111.1	111.2	111.1	111.6	111.7	94.5	85.5	132.1	107.70
4	119.65	118.4	111.6	112.1			112.1		36.4		119.43
5			109.9	111.7							
6			118.5	109.9							
7				118.6							

① 化合物 14～19[C_6F_6]。



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$\overset{n+3}{C}F_3(CF_2)_n\overset{2}{C}F_2-\overset{1}{C}F_2-I$　　$\overset{4}{C}F_3(CF_2)_n\overset{3}{C}F_2\overset{2}{C}F_2\overset{1}{C}F_3$　　$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}Cl_3$

14. $n=1$　　17. $n=1$　　20

15. $n=2$　　18. $n=2$

16. $n=3$　　19. $n=3$

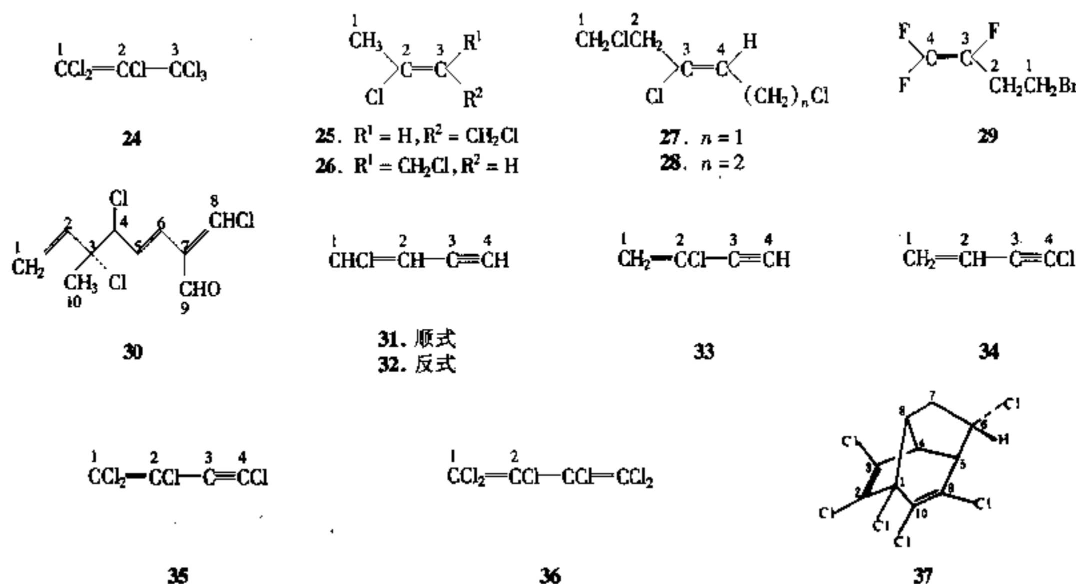
$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}Cl_2-\overset{4}{C}H_3$　　$\overset{1}{C}Cl_3\overset{2}{C}Cl=\overset{3}{C}Cl_2$　　$BrF_2\overset{4}{C}-\overset{3}{C}FCl(F)>\overset{2}{C}=\overset{1}{C}<H(H)$

21　　22　　23

表 18-3 脂肪卤族化合物 24～37 的 ^{13}C-NMR 化学位移数据[5,7,9～12]①

C \ 化合物	24	25	26	27	28	29	30	31	32	33	34	35	36	37
1	128.1	25.8	20.5	41.0	41.1	26.86	116.3	130.9	133.0	124.5	129.4	129.5	127.0	81.22
2	132.5	135.2	136.0	41.6	41.9	30.36	122.5	112.4	114.0	120.1	116.8	112.9	124.2	127.67
3	93.3	121.6	123.2	134.6	130.7	127.70	71.5	87.5	82.1	81.2	69.2	63.9		138.08
4		39		124.3	126.7	155.15	69.5	78.1	79.2	80.3	68.6	79.8		53.62
5				39.3	30.9		134.0							55.76
6					25.5		139.5							63.44
7					43.7		137.3							33.88
8							143.9							59.82
9							189.3							134.07
10							24.6							126.58
R		39.9	39.4											

① 化合物 31～34 在 $(CD_3)_2CO$ 中测定。



二、芳香卤族化合物的 ^{13}C-NMR 化学位移

表 18-4 芳香卤族化合物 38～51 的 ^{13}C-NMR 化学位移数据[13～17]①

C \ 化合物	38	39	40	41	42	43	44	45	46	47	48	49	50	51
1	122.8	138.5	132.2	118.7	121.3	115.3	118.9	124.7	163.6	156.2	161.9	166.3	153.31	115.7
2	159.9	113.9	129.3	128.1	134.6	127.7	127.2	128.5	115.5	114.2	116.9	116.6	141.31	132.6
3	113.8	159.9	114.0	126.5	127.3	127.3	135.2	126.6	130.4	115.6	130.2	126.5	113.58	137.8
4	126.6	110.3	159.6	123.2	123.6	133.3	123.3	132.7	124.5	148.3	129.7	144.9	124.77	
5	122.8	128.4			123.6		126.9							
6	130.6	123.8			129.0		132.2							

① 化合物 38～40 在 $(CH_3)_2SO$ 中测定；化合物 41～45 在 C_2H_5OH 中测定；化合物 50 在 $(CD_3)_2CO$ 中测定；化合物 51 在 CS_2 中测定。

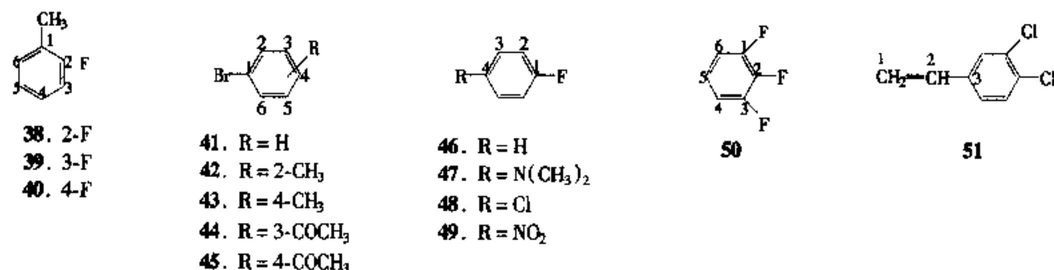
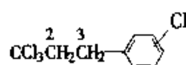


表 18-5 芳香卤族化合物 52～64 的^{13}C-NMR 化学位移数据[1,2,18,19]①

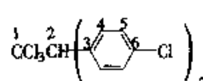
C \ 化合物	52	53	54	55	56	57	58	59	60	61	62	63	64
1	99.0	99.0	100.9	73.9	148.89	148.11	111.43	127.18	130.56	137.18	132.71	123.34	100.02
2	54.5	56.4	69.8	60.8	129.6	130.09	161.38	131.87	120.14	91.80	128.19	132.12	139.87
3	30.9	32.1	134.0	133.5	156.47	160.03	116.73	127.18	129.76	134.90	128.19	128.85	129.74
4			129.0	128.8	113.75	112.77	131.39	130.51	130.65	130.31	124.41	127.97	134.31
5			131.0	129.7	129.23	128.15	131.49	132.56	132.79	132.80	132.61	133.77	135.52
6			136.0	137.5	119.06	120.16	128.68	128.51	128.63	128.49			
7					27.08	28.81	126.02	127.00	127.23	127.24			
8					30.00	33.28	127.77	127.78	127.80	127.44			
9						25.46	128.05	127.78	127.80	127.44			
10							135.13	134.90	135.42	135.73			

① 化合物 58～64 在$(CD_3)_2CO$ 中测定。

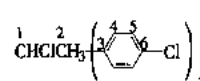


52. *o*-Cl

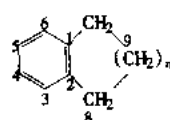
53. *p*-Cl



54

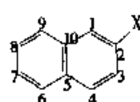


55



56. *n* = 0

57. *n* = 1

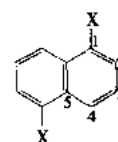


58. X = F

59. X = Cl

60. X = Br

61. X = I



62. X = Cl

63. X = Br

64. X = I

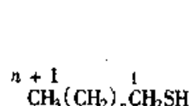
第二节 含硫化合物的^{13}C-NMR 化学位移

一、硫醇和硫醚化合物的^{13}C-NMR 化学位移

表 18-6 硫醇和硫醚 1～13 的^{13}C-NMR 化学位移数据[20-22]①

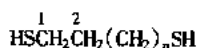
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13
1	26.4	24.6	28.6	22.75			24.7	24.78	19.3	25.5	34.3	29.63	29.20
2	27.6	37.1		37.51	106.73	105.43	38.8	36.02		14.8	23.2	30.83	30.83
3	12.6	22.3					22.5	30.48			13.7	34.95	32.15
4		13.9			70.10	70.55	13.6	29.44				61.12	28.58
5					42.18	39.63							61.12
7					32.64	32.47							
8					16.99	16.99							

① 化合物 1,2,7 在 CD_3OD 中测定；化合物 3,4,8,12,13 在 C_6D_6 中测定。



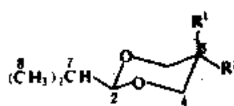
1. *n* = 1

2. *n* = 2



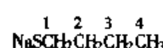
3. *n* = 0

4. *n* = 1

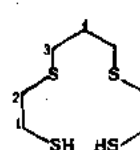


5. $R^1 = SCH_3, R^2 = H$

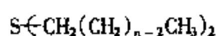
6. $R^1 = H, R^2 = SCH_3$



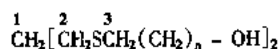
7



8



9. $n=1$
10. $n=2$
11. $n=3$



12. $n=1$
13. $n=2$

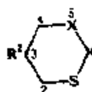
表 18-7 硫醚化合物 14～27 的 ^{13}C-NMR 化学位移数据[23～26]

C \ 化合物	14	15	16①	17①	18	19	20	21	22	23	24	25	26	27
1	59.8	58.6								34.25	35.94			
2	28.9	31.0	29.1	41.1	28.9	41.9	37.33	35.83	28.80	34.02	39.90	68.5	98.9	95.1
3	30.3	31.5	27.8	29.7	26.2	26.8	36.61	33.16	36.01	34.13	38.70	27.0	30.2	29.3
4	70.0	72.1	26.5	39.3			26.36	34.86	32.31	31.16	36.70			
5				33.8			29.36	27.77		26.79	28.84		26.0	31.9
6				28.7	30.9	31.5	21.87	28.45		14.26	20.10		65.1	64.3
R				28.3		27.5	21.87	22.68	23.01	17.53	20.55			21.5
R^1													55.3	54.6

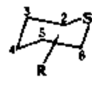
① 化合物 16,17 在 $(CD_3)_2SO$ 中测定。



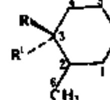
14. $R = H, R^1 = OCOC_6H_5$
15. $R = OCOC_6H_5, R^1 = H$



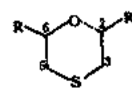
16. $X = CH_2, R = H$
17. $X = CH_2, R = CH_3$
18. $X = S, R = H$
19. $X = S, R = CH_3$



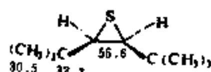
20. $R = 2\text{-}CH_3$
21. $R = 3\text{-}CH_3$
22. $R = 4\text{-}CH_3$



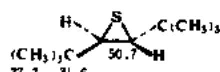
23. $R = H, R^1 = CH_3$
24. $R = CH_3, R^1 = H$



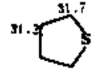
25. $R = R^1 = H$
26. $R = H, R^1 = OCH_3$
27. $R = CH_3, R^1 = OCH_3$



28[27]



29[27]



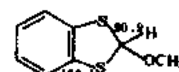
30[20]



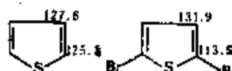
31[20]



32[28]



33[28]



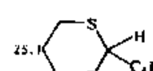
34[29] 35[29]



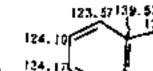
36[29]

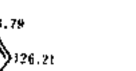


37[29]

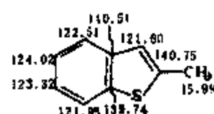


38[33]

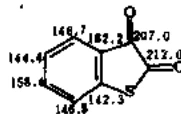




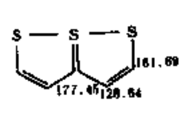
39[30]



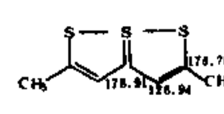
40[30]



41[31]



42[32]

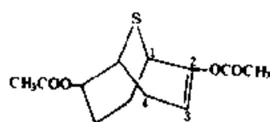


43[32]

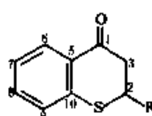
表 18-8　硫醚化合物 44～57 的^{13}C-NMR 化学位移数据[34～38]

C \ 化合物	44	45	46	47	48	49	50	51	52	53	54	55①	56①	57①
1	33.08											114.58	110.63	115.47
2		26.6	36.2	137.9	151.0	209.0	185.4					132.18	134.70	131.66
3	113.08	39.5	47.6	126.6	124.6	136.0	126.0	193.9	193.3	215.6	214.8	134.26	119.20	132.66
4	31.54	193.8	193.9	179.4	179.9	131.4	143.7	117.7	131.8	136.0	134.4	130.54	134.70	131.66
5	20.90	130.9	130.2	132.2	130.5	128.0	126.2	170.2	150.1	172.8	173.0	128.74	115.16	129.03
6		129.1	128.8	128.5	128.2	130.3	130.0	132.4	133.9	131.7	124.0	126.72	146.30	133.26
7		124.9	124.6	125.7	125.9	123.4	124.2	126.4	127.5	126.9	128.5			
8		133.1	133.1	131.4	131.2	134.4	131.6	129.4	128.7	129.6	114.9			
9		127.5	127.3	127.7	127.3	127.7	126.5	131.8	128.7	132.2	162.9			
10		142.1	141.6	137.5	137.4	140.3	137.7							
R											55.6			

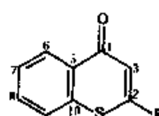
① 化合物 55～57 在 CCl_4 中测定。



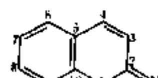
44



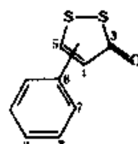
45. R = H
46. R = CH_3



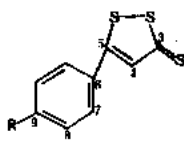
47. R = H
48. R = CH_3



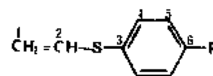
49. X = S
50. X = O



51. 5 位
52. 4 位



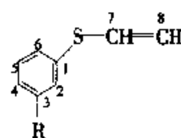
53. R = H
54. R = OCH_3



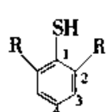
55. R = H
56. R = NH_2
57. R = Cl

表 18-9　硫醚化合物 58～71 的^{13}C-NMR 化学位移数据[39～42]

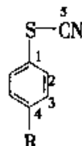
C \ 化合物	58	59	60	61	62	63	64	65	66	67	68	69	70	71
1	135.2	135.1	138.0	130.7	127.0	124.8	121.4	123.9	138.6	129.2	137.3	137.8	138.6	135.1
2	131.3	131.9	130.1	128.9	134.3	131.0	131.7	132.7	126.8	130.3	128.2	136.0	127.9	127.8
3	129.9	139.5	135.8	129.2	128.8	130.7	131.1	131.2	128.8	114.8	128.9	129.9	138.5	129.6
4	127.7	128.4	127.8	125.4	134.5	130.7	140.8	136.5	125.0	158.5	131.1	124.8	126.1	134.9
5		129.9	131.0			111.9	111.6	110.9				125.4	128.8	
6		128.8	128.4									126.6	124.3	
7	132.5	133.2	131.5						15.9	17.9	16.1	19.9	21.2	20.8
8	116.3	115.8	118.4									16.0	16.1	16.5
R		22.5					21.9			55.3				



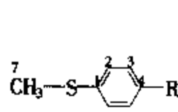
58. R = H
59. R = CH_3
60. R = Cl



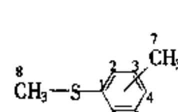
61. R = H
62. R = CH_3



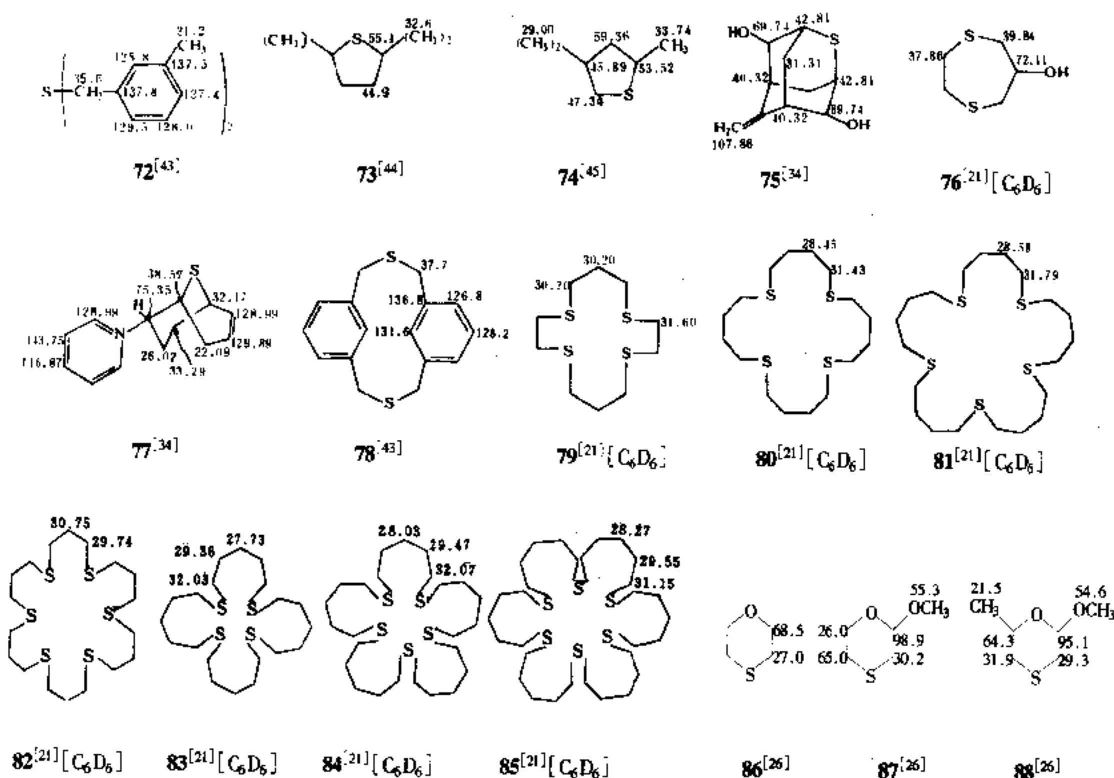
63. R = H
64. R = CH_3
65. R = Cl



66. R = H
67. R = CH_3O
68. R = Cl



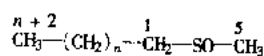
69. 2-CH_3
70. 3-CH_3
71. 4-CH_3



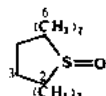
二、亚砜类和砜类化合物的^{13}C-NMR化学位移

表 18-10 亚砜类化合物 89～102 的^{13}C-NMR化学位移数据[20,27,44,46～48]

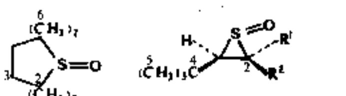
C \ 化合物	89	90	91	92	93	94	95	96	97	98	99	100	101	102
1	58.5	54.4												73.7
2	16.1	24.5	63.2	71.4	63.8	54.3	48.2							38.7
3	13.3	22.0	39.4			25.4	18.2				49.5	48.7	48.8	
4		13.7		31.8	33.2		24.5	67.6	80.2	89.2	13.6	14.3	14.8	21.3
5	38.6	38.6		30.8	29.5				70.9	75.6	24.5	32.0	31.9	
6			26.0 21.8								58.3	65.2	69.9	
R									18.7	26.4				



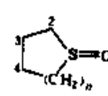
89. $n=1$
90. $n=2$



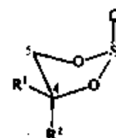
91



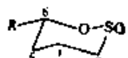
92. $R^1 = H, R^2 = C(CH_3)_3$
93. $R^1 = C(CH_3)_3, R^2 = H$



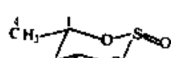
94. $n=1$
95. $n=2$



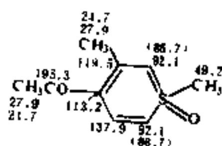
96. $R^1 = R^2 = H$
97. $R^1 = CH_3, R^2 = H$
98. $R^1 = R^2 = CH_3$



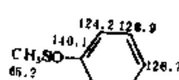
99. R = H
100. $R = CH_3$
101. $R = C_6H_5$



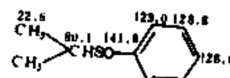
102



103[49]



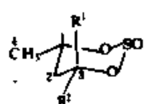
104[50]



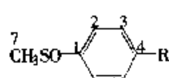
105[50]

表 18-11 亚砜类化合物 106 ~ 115 的 ^{13}C-NMR 化学位移数据[35,42,48,50]

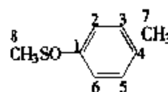
C \ 化合物	106	107	108	109	110	111	112	113	114	115
1	64.6	62.2	146.3	137.4	154.0	144.2	145.9	143.4	89.5	145.7
2	40.7	37.9	123.6	125.5	124.9	134.0	123.7	123.7	141.6	124.7
3	64.6	71.5	129.4	115.0	124.6	130.7	139.4	130.1	123.2	129.2
4	21.1	21.0	131.0	162.2	150.1	130.6	131.6	141.5	128.8	131.0
5						127.5	129.2		125.9	
6						123.1	120.6		33.4	
7			44.0	44.0	42.2	18.4	21.3	21.3	23.6	
8						42.2	43.9	44.1		
R	21.1	22.4		55.6						



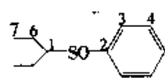
106. $R^1 = H, R^2 = CH_3$
107. $R^1 = CH_3, R^2 = H$



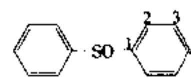
108. R = H
109. $R = OCH_3$
110. $R = NO_2$



111. $2\text{-}CH_3$
112. $3\text{-}CH_3$
113. $4\text{-}CH_3$



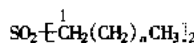
114



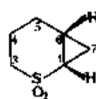
115

表 18-12 砜类化合物 116 ~ 129 的 ^{13}C-NMR 化学位移数据[20,35,42,52]

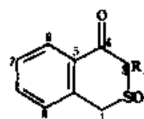
C \ 化合物	116	117	118	119	120	121	122	123	124	125	126	127	128	129
1	42.6	46.2	54.5	34.9	55.5	50.1		141.0	132.5	146.9	139.6	141.1	138.5	141.6
2		6.6	15.5				148.2	127.2	129.5	128.9	137.8	127.7	127.5	127.6
3			13.2	51.7	62.4	68.2	138.6	129.3	114.6	124.6	132.4	139.7	130.0	129.3
4				21.2	186.5	192.5	72.8	133.5	163.8	151.3	133.6	134.4	144.6	133.2
5				18.1	130.9	129.5					126.9	129.3		
6				17.5							129.3	124.5		
7				10.2	135.6	134.6		44.3	44.8	44.3	20.0	21.2	21.5	
8					132.7	131.1					43.7	44.5	44.6	
R									55.7					



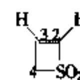
116. $n = 1$
117. $n = 2$
118. $n = 3$



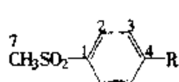
119



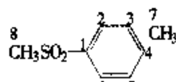
120. R = H
121. $R = CH_3$



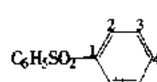
122



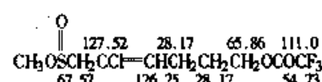
123. R = H
124. $R = CH_3O$
125. $R = NO_2$



126. $2\text{-}CH_3$
127. $3\text{-}CH_3$
128. $4\text{-}CH_3$



129

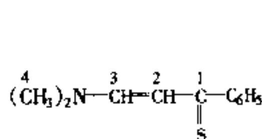


130[53]

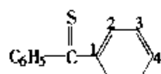
三、硫酮、硫胺、硫脲和其他含硫化合物的^{13}C-NMR 化学位移

表 18-13　硫酮等化合物 131～144 的^{13}C-NMR 化学位移数据[27,35,54～59]

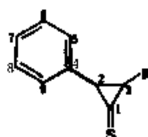
C \ 化合物	131	132	133	134	135	136	137	138	139	140	141	142	143	144
1	211	147.2	181.4	177.6	37.2	45.0	43.2	125.78	34.9	43.3		38.3	30.7	180.8
2	111	129.5	160.4	153.4	45.4	45.6	43.2		49.3	48.9	76.2	23.9	20.0	
3	157.5	127.9	159.3	153.4	188.1	175.1	194.0	156.83		21.3		23.5	19.9	
4	38.5 46.4	131.9	122.4	122.4				110.34	182.9	179.6	34.2	30.7	26.1	
5			131.9	132.1				184.52			30.8	53.3	42.6	
6			129.5	129.5				169.41			27.6			
7			133.9	133.9				25.87						
8														
R			11.6											



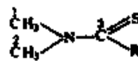
131



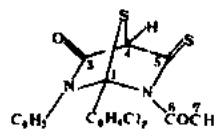
132



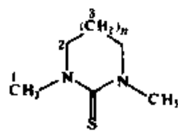
133. R = CH_3
134. R = C_6H_5



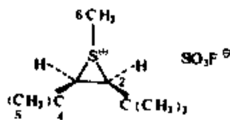
135. R = H
136. R = Cl
137. R = $N(CH_3)_2$



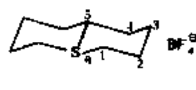
138



139. n = 0
140. n = 1



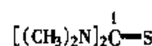
141



142



143

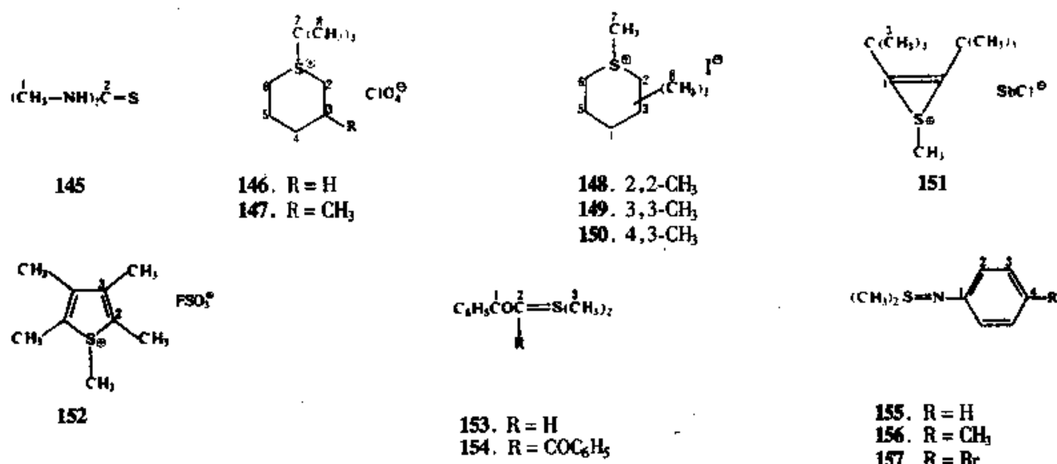


144

表 18-14　硫胺及硫脲化合物 145～157 的^{13}C-NMR 化学位移数据[55,60～64]①

C \ 化合物	145	146	147	148	149	150	151	152	153	154	155	156	157
1	30.9						115.11		182.3	190.9	154.9	152.0	154.4
2	182.7	33.6	38.1	50.6	51.1	33.9	34.00	28.4	53.2	88.2	117.8	118.3	119.3
3		23.7	30.7	35.3	32.2	32.1	30.60	148.5	28.7	26.9	128.8	129.5	131.3
4		23.7	31.9	19.9	36.6	28.4					116.4	125.8	107.4
5		23.7	23.4	19.6	20.1	32.1							
6		33.6	32.4	35.1	40.4	33.9							
7		56.0	55.9	17.8	25.8	20.8							
8		25.3	25.1	25.9 23.1	33.3 25.7	28.0 26.8							
R			25.1										

① 化合物 146～150 在 D_2O 中测定；化合物 151 在 CH_2Cl_2 中测定；化合物 152 在 FSO_3H 中测定。



第三节　膦化合物的^{13}C-NMR 化学位移

一、膦化合物的^{13}C-NMR 化学位移

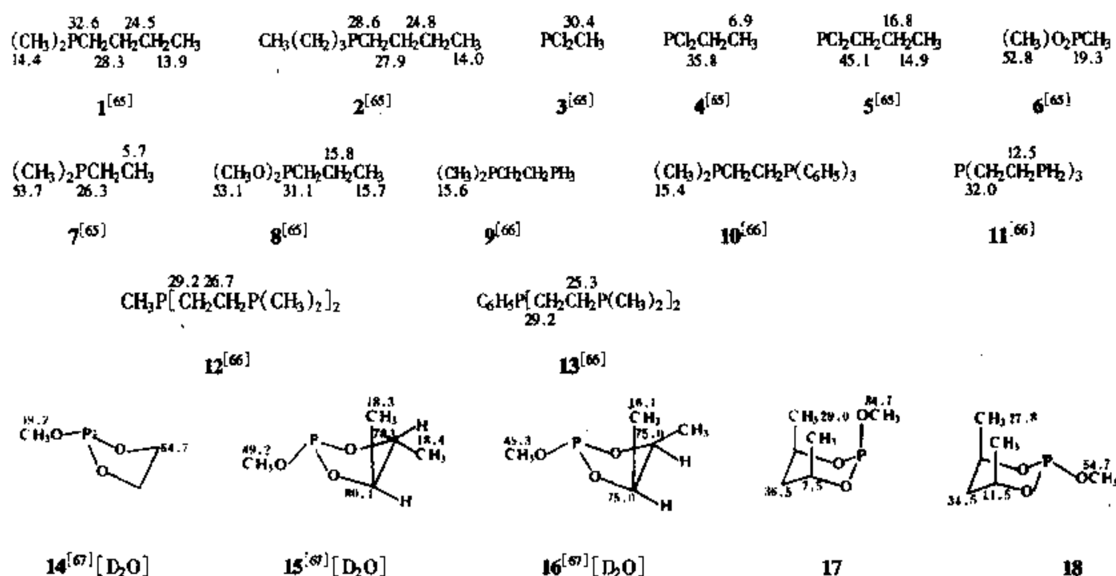
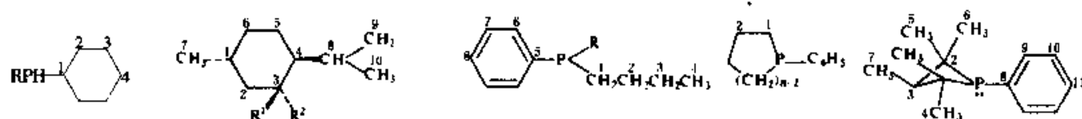


表 18-15　膦化合物 19～31 的^{13}C-NMR 化学位移数据[69,70]

C ＼ 化合物	19	20	21	22	23	24	25	26	27	28	29	30	31
1	27.2	39.3	48.5	34.0	27.7	28.52	27.86	11.04	27.15	24.79	29.89		
2	36.0	28.9	25.6	37.9	39.5	28.40	28.12		27.74	23.65	25.16	34.52	30.22
3	27.4	27.0	26.0	38.2	35.8	24.48	24.14			28.04	28.27	49.70	54.02
4	25.9	26.0	25.8	45.7	50.3	13.82	13.74						
5				25.9	26.4	139.78	139.39					20.92	26.24
6				35.3	36.3	132.44	132.57					32.71	26.52
7				22.6	22.7	128.20	128.18					8.12	9.96
8				28.5	30.1	128.43	128.12					140.09	137.71
9				15.5	22.4							129.50	135.11
10				21.7	21.2							127.64	127.57
11												126.15	128.16
R		11.3											



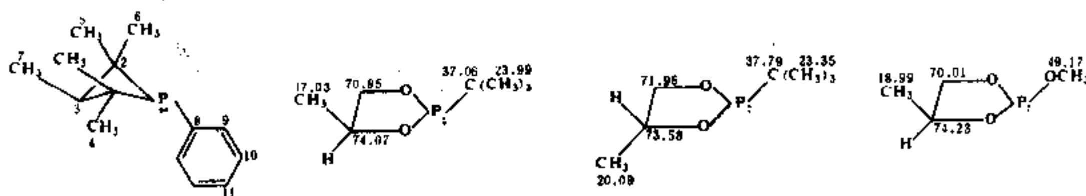
19. R = H
20. R = CH_3
21. R = Cl

22. $R^1 = H, R^2 = P(C_6H_5)_2$
23. $R^1 = P(C_6H_5)_2, R^2 = H$

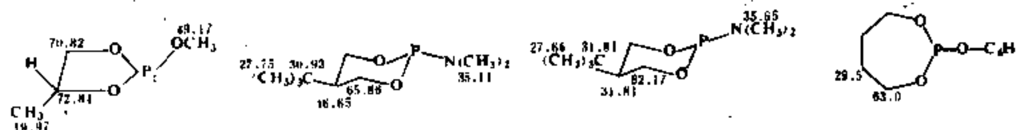
24. R = $CH_3(CH_2)_3$
25. R = C_6H_5

26. $n = 1$
27. $n = 3$
28. $n = 4$
29. $n = 5$

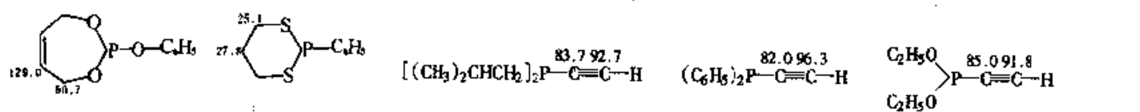
30



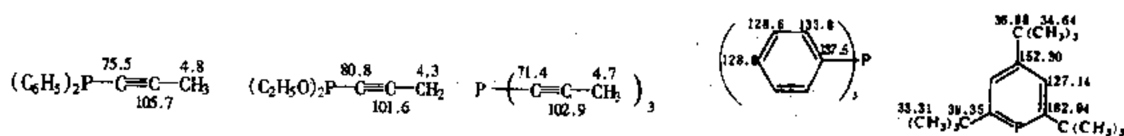
31 32[71] 33[71] 34[71]



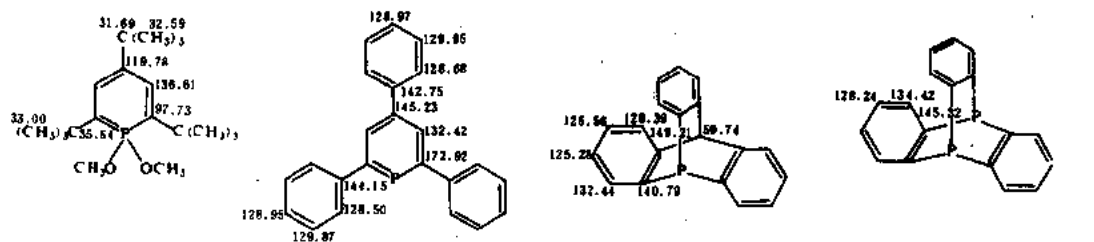
35[71] 36 37 38[73]



39[73] 40[33] 41[74] 42[75] 43[75]



44[75] 45[75] 46[75] 47[76] 48[77]



49[77] 50[77] 51[76] 52[78][CS_2]

二、氧化膦类化合物的^{13}C-NMR化学位移

表 18-16　氧化膦化合物 53～66 的^{13}C-NMR 化学位移数据[65,79～84]①

C \ 化合物	53	54	55	56	57	58	59	60	61	62	63	64	65	66
1	27.8	30.9	11.59	67.61	19.1	28.2	25.8	43.36	34.30	135.0	134.2	62.44	26.1	30.0
2	24.0	24.6	61.63	62.54	6.8	16.7	25.2	62.98	62.31	129.0	130.1	16.29	35.2	35.1
3	24.4	24.0	16.97	17.02		15.4	24.0	16.74	16.60	128.6	129.7	29.64	95.7	95.8
4	13.6	13.6					13.8			131.5	134.7		14.4	18.9
R										18.0				

① 化合物 65～66 在 H_2O 中测定；化合物 57～59 在 $(CH_3)_2CO$ 中测定。

$X\text{—}P(\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3)_3$

53. X = O
54. X = S

$(\overset{3}{C}H_3\overset{2}{C}H_2O)_2P(O)\overset{1}{C}H_2R$

55. R = H
56. R = OCH_3

$\overset{n+1}{C}H_3(\overset{1}{C}H_2)_n\text{—}P(O)\text{—}(OCH_2CH_3)_2$

57. n = 1
58. n = 2
59. n = 3

$(\overset{3}{C}H_3\overset{2}{C}H_2O)_2P(O)\overset{1}{C}H_2COR$

60. R = H
61. R = OCH_3

62. R = CH_3
63. R = Cl

$(\overset{2}{C}H_3\overset{1}{C}H_2O)_2P(O)\overset{3}{C}HN_2$

64

65. X = O
66. X = S

67[85]　（20.02, 20.02, 53.34, 26.11, 32.17, 48.19, 26.11）

68[85]　（19.40, 54.47, 20.45, 28.73, 31.97, 47.86, 26.24）

表 18-17　氧化膦及硫化膦化合物 69～82 的^{13}C-NMR 化学位移数据[70,82,86～88]

C \ 化合物	69	70	71	72	73	74	75	76	77	78	79	80	81	82
1			30.30	28.73	31.76	29.30								
2	150.0	151.3	25.72	22.54	21.66	20.21	30.1	30.8	28.0	29.2	26.9	30.5	18.8	20.9
3	125.2	137.1		26.98	29.56	27.24	53.5	55.0	29.3	35.4	28.8	37.3	28.6	22.3
4	137.8	136.4				23.38			66.1	70.6	65.5	70.1	27.4	27.4
5									17.3	21.6	19.0	17.4		
6							20.4	17.5						
7	71.6	71.5											28.5	
8	24.1	24.5												
R		19.9												

69. R = H
70. R = CH_3

71. n = 1
72. n = 2
73. n = 3
74. n = 4

75

76

77. R = H
78. R = CH_3

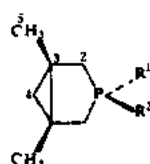
79. R = H
80. R = CH_3

81. n = 1
82. n = 2

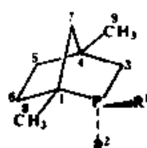
表 18-18　氧化膦化合物 83～96 的^{13}C-NMR 化学位移数据[75,89～93]

C \ 化合物	83	84	85	86	87	88	89	90	91①	92①	93	94	95	96
1			43.4	45.2	28.5	30.8	77.9	74.3						
2	39.9	38.6			26.3	42.8	95.3	105.3	127.9	123.4	37.48	36.14	31.4	30.1
3	26.0	24.8	40.0	41.5	21.6	208.3	131.4	133.2	147.3	150.0	132.71	132.17	112.9	113.8
4	25.0	26.3	43.8	43.2			130.7	130.5	31.6	36.8			144.6	143.5
5	19.3	19.6	37.5	36.9			128.6	128.3	30.3	31.9				
6			31.5	31.1	29.7	29.1	132.5	131.8	22.8	23.7	14.53	12.75		
7			50.1	50.4	20.9	17.1								
8			14.9	13.9										
9			24.1	23.5									39.9	40.8
R								4.7			15.24	6.12	13.6	9.6

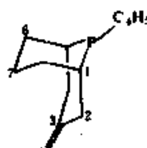
① 化合物 91～92 在 C_6F_6 中测定。



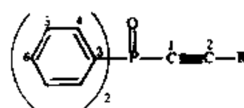
83. $R^1 = C_6H_5, R^2 = O$
84. $R^1 = O, R^2 = C_6H_5$



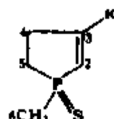
85. $R^1 = C_6H_5, R^2 = O$
86. $R^1 = O, R^2 = C_6H_5$



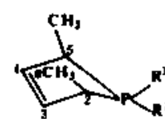
87. $X = H_2$
88. $X = O$



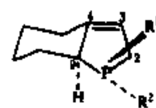
89. R = H
90. $R = CH_3$



91. R = H
92. R = Cl



93. $R^1 = O, R^2 = CH_3$
94. $R^1 = CH_3, R^2 = O$

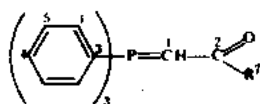


95. $R^1 = O, R^2 = CH_3$
96. $R^1 = CH_3, R^2 = O$

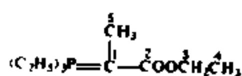
三、鏻炔、鏻盐、鏻酯和其他含磷化合物的^{13}C-NMR 化学位移

表 18-19　鏻炔等化合物 97～110 的^{13}C-NMR 化学位移数据[94～96]

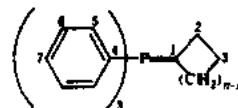
C \ 化合物	97	98	99	100	101	102	103	104	105	106	107	108	109	110
1	51.3	29.8	32.96	31.68	4.3	14.6	78.3	28.7	117.9	117.1	0.4	25.4	29.5	29.8
2	190.5	172.0		175.13	7.7	28.6	117.2	137.9	133.6	134.4	4.9	23.1	28.0	26.4
3	127.4	128.2	57.91	57.36		22.8	114.6	90.7	130.5	130.9		20.3	26.4	25.1
4	133.0	133.2	15.45	14.18		131.8	126.6	131.2	135.0	135.3				25.4
5	128.7	129.0	12.15	12.98	132.8	132.5	134.0	133.1	17.0	35.3	118.3	118.0	118.5	117.3
6	131.8	130.1			128.8	128.6	129.2	128.7	6.9	28.2	133.7	133.8	133.7	134.4
7	28.4	49.7			130.8	130.7	133.1	131.3			130.4	130.7	130.3	130.6
8											135.2	135.2	134.8	134.9



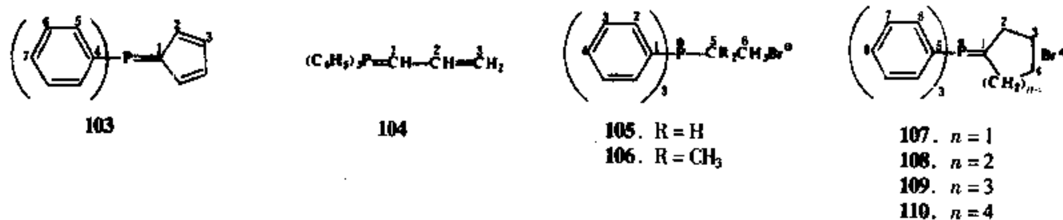
97. $R = CH_3$
98. $R = OCH_3$



99. *cis*
100. *trans*



101. *n* = 1
102. *n* = 2

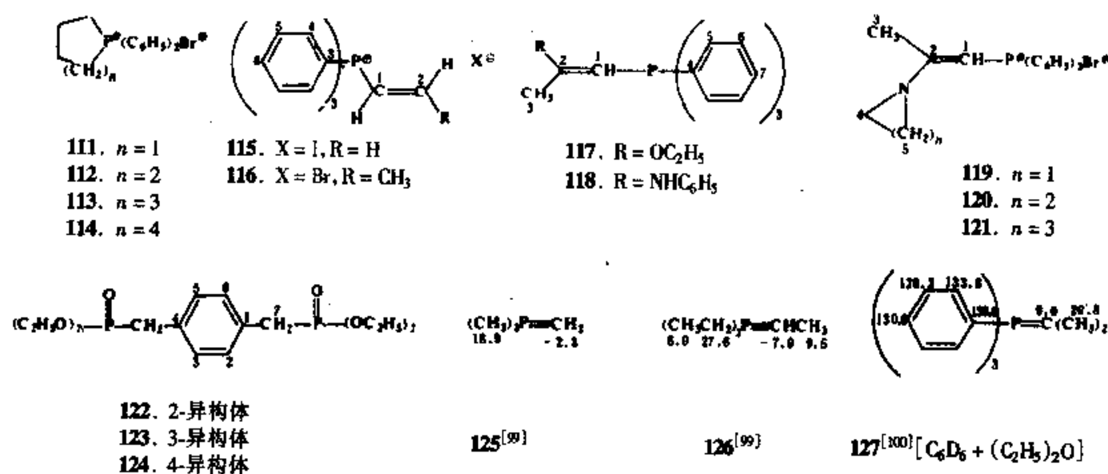


103　104　105. R = H　106. R = CH_3　107. $n=1$　108. $n=2$　109. $n=3$　110. $n=4$

表 18-20　鏻盐等化合物 111～124 的 ^{13}C-NMR 化学位移数据[70,80,96～98]

C \ 化合物	111	112	113	114	115	116	117	118	119	120	121	122①	123①	124①
1	25.42	20.4	22.89	19.97	119.2	110.1	76.5	60.8	80.7	54.3	57.2	131.9	133.1	131.6
2	26.19	21.75	22.05	20.21	145.2	159.5	178.9	163.2	175.8	164.1	162.7		131.9	130.6
3		24.12	27.70	26.58	117.2	118.0	20.6	21.4	22.2	17.5	22.1	131.9		
4				22.74	133.9	133.7	120.9	122.6	28.6	51.5 49.5	52.2	127.3	128.7	
5					130.7	130.5	133.0	133.0			25.5 24.9		128.7	
6					135.5	135.2	130.0	130.1						
7							134.2	134.0				31.3	33.6	33.5
R						21.7								

① 化合物 122～124 在 $(CD_3)_2CO$ 中测定。



111. $n=1$　112. $n=2$　113. $n=3$　114. $n=4$

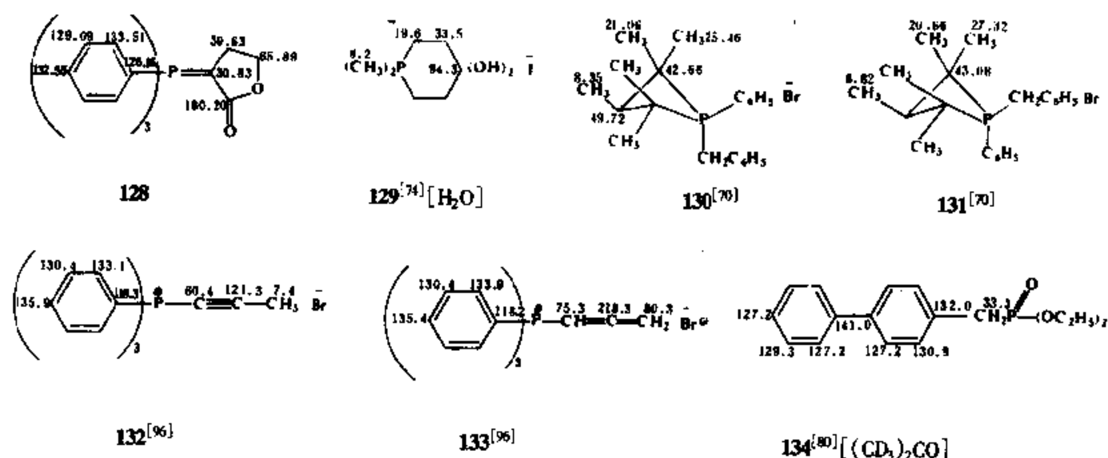
115. X = I, R = H　116. X = Br, R = CH_3

117. R = OC_2H_5　118. R = NHC_6H_5

119. $n=1$　120. $n=2$　121. $n=3$

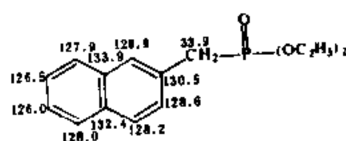
122. 2-异构体　123. 3-异构体　124. 4-异构体

125[99]　126[99]　127[100] [C_6D_6 + $(C_2H_5)_2O$]

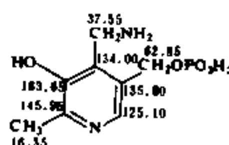


128　129[74] [H_2O]　130[70]　131[70]

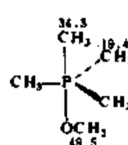
132[96]　133[96]　134[80] [$(CD_3)_2CO$]



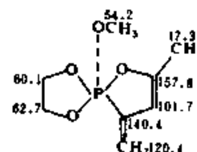
135[80] [$(CD_3)_2CO$]



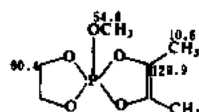
136[72]



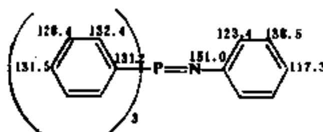
137



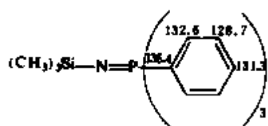
138[51]



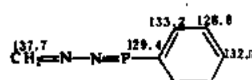
139[51]



140[68]



141[8]



142[68]

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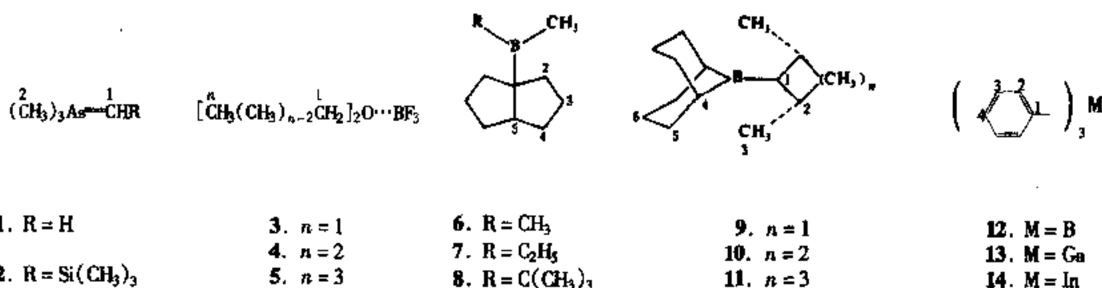
第十九章 有机金属化合物与离子化合物的^{13}C-NMR 化学位移

第一节 有机金属化合物的^{13}C-NMR 化学位移

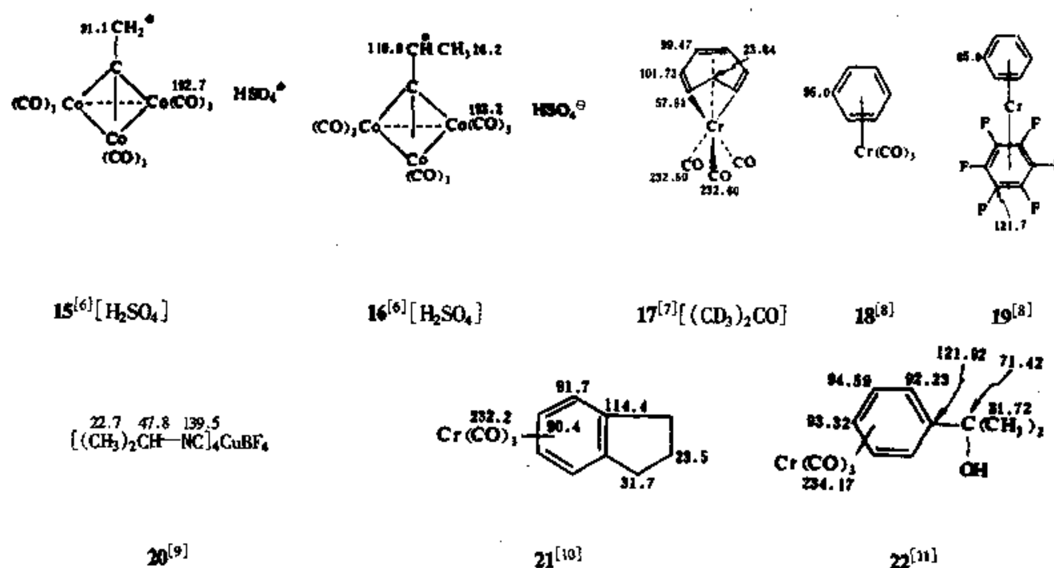
一、砷和硼化合物的^{13}C-NMR 化学位移

表 19-1 砷和硼化合物 1～14 的^{13}C-NMR 化学位移数据[1~5]

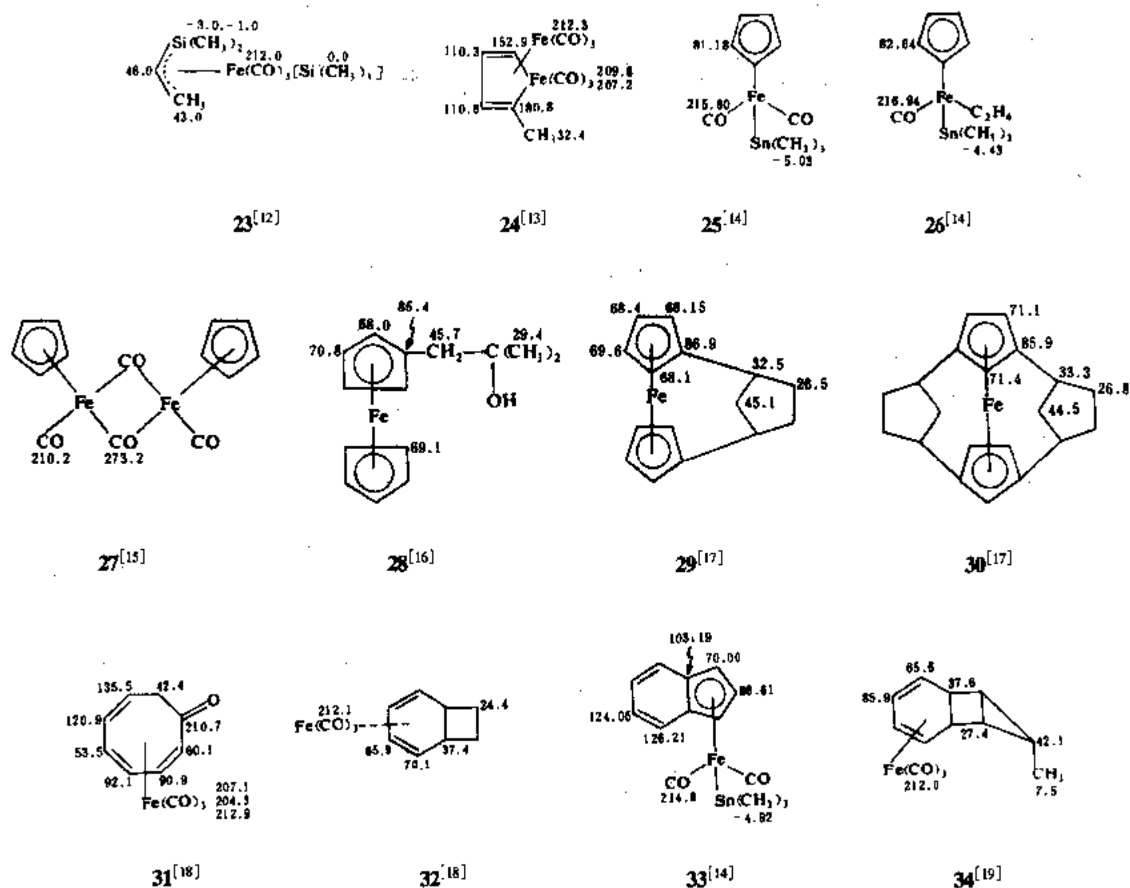
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	7.6	8.0	60.0	66.1	72.1				52.0	55.1	54.0	143.2	147.3	
2	15.6	17.1		15.5	22.8	36.9	36.8	36.8	29.1	35.8	33.1	138.5	137.9	138.4
3					10.4	26.4	26.3	26.3	23.5	22.3	24.6	127.4	128.2	128.5
4						35.0	35.1	35.0	30.0	31.5	31.7	131.3	129.8	129.2
5						45.9	45.5	46.7	33.2	33.1	34.1			
6									23.4	23.3	23.8			
R		5.0												



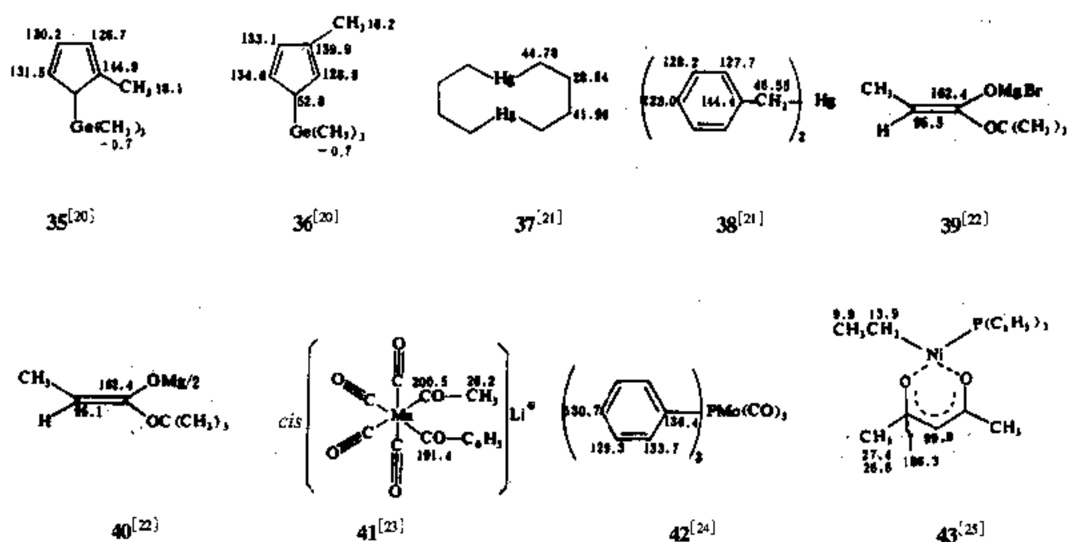
二、钴、铬和铜化合物的^{13}C-NMR 化学位移



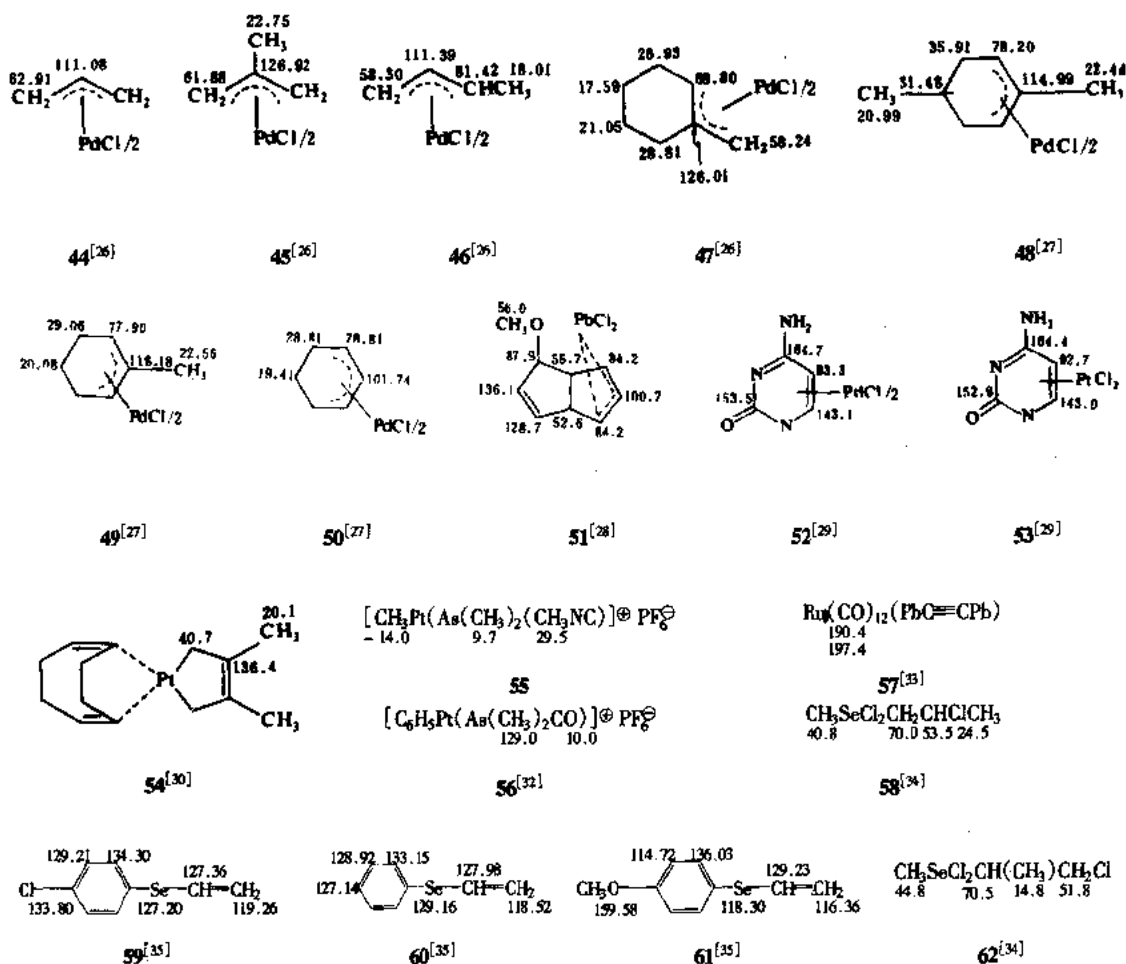
三、铁化合物的^{13}C-NMR化学位移



四、锗、汞、锰、镁、钼和镍化合物的^{13}C-NMR化学位移



五、钯、铂、铅和硒化合物的^{13}C-NMR化学位移

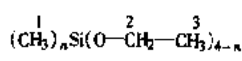


六、硅化合物的^{13}C-NMR化学位移

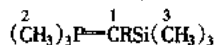
表 19-2 硅化合物 63～76 的^{13}C-NMR化学位移数据[36～40]①

C \ 化合物	63	64	65	66	67	68	69	70	72	72	73	74	75	76
1	-6.92	-3.14	-0.47		18.9	18.5			26.39	27.90	24.75	35.04	0.7	0.3
2	58.34	57.98	57.84		58.6	58.3	23.1	20.4	27.49	28.75	30.87	33.66	20.0	21.4
3	18.45	18.61	18.69	-3.0	-3.2	-6.0	28.4	29.6	28.35	28.31	28.98	30.06	4.8	6.7
4				31.6	31.3	28.7	9.0	9.0	27.14	27.06	26.93	26.75		
5							17.3	15.6	-3.56	-4.50	-11.92	-5.31		
R^1							-2.3							

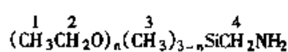
① 化合物 63～65 在 C_6D_6 中测定。



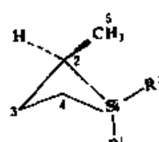
63. $n=1$
64. $n=2$
65. $n=3$



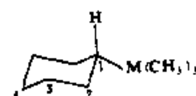
75. R = H
76. R = $Si(CH_3)_3$



66. $n=0$
67. $n=1$
68. $n=2$



69. $R^1=CH_3, R^2=H$
70. $R^1=H, R^2=CH_3$



71. M = Si　73. M = Sn
72. M = Ge　74. M = Pb

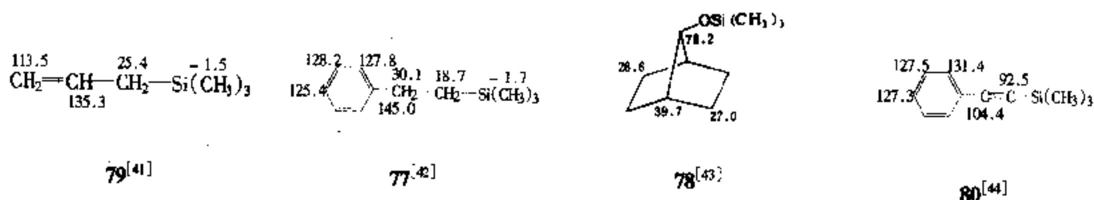
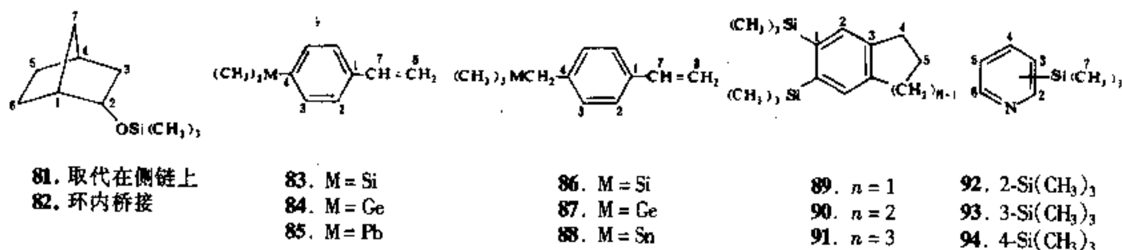


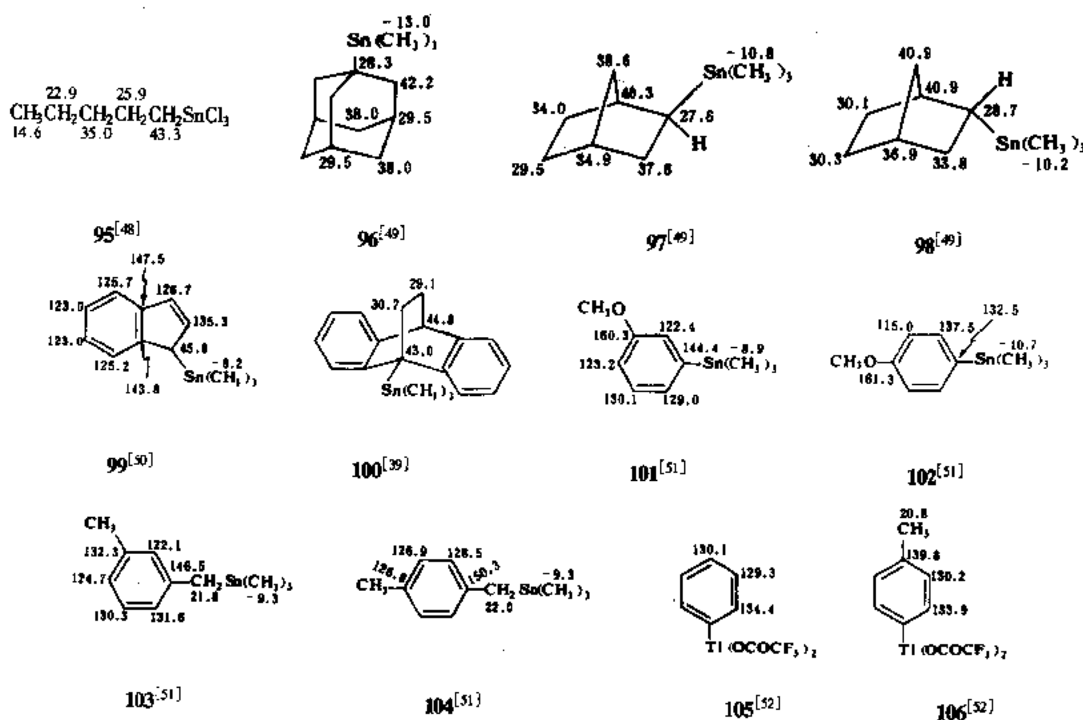
表 19-3 硅化合物 81～94 的^{13}C-NMR 化学位移数据[43,45～47]

C \ 化合物	81①	82①	83	84	85	86	87	88	89	90	91	92	93	94
1	43.8	42.1	137.78	137.29	136.72	133.44	133.39	132.73	144.3	143.4	142.4			
2	73.4	71.2	125.37	125.56	126.13	125.97	126.00	126.18	129.1	131.6	136.8	168.2	152.5	147.0
3	41.2	38.4	133.15	132.73	136.29	127.77	127.35	126.47	145.9	143.9	136.9	128.3	132.8	126.1
4	35.5	37.7	139.27	141.41	148.05	139.50	140.40	142.17	30.2	32.9	29.3	133.5	138.9	147.8
5	28.6	29.9								24.9	23.3	122.5	121.4	
6	24.7	20.1							2.41	2.20	2.00	150.1	148.6	
7	35.5	40.1	136.98	136.98	137.06	136.79	136.79	136.76				-1.8	-3.0	-3.8
8			113.45	113.22	113.00	111.62	111.54	111.22						
9														

① 化合物 81～82 在 CCl_4 中测定。



七、锡和铊化合物的^{13}C-NMR 化学位移



第二节　离子化合物的^{13}C-NMR 化学位移

一、阳碳离子化合物的^{13}C-NMR 化学位移

表 19-4　阳碳离子化合物 1 ~ 14 的^{13}C-NMR 化学位移数据[53 ~ 59]①

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	51.5	47.5	44.6	57.6	281.7	64.7	36.2	33.5	231.3	268.2	43.7	30.7	234.7	212.5
2	320.6	335.2	335.4	108.2	56.4	61.7	32.5	38.9	147.0	146.7	269.0	231.0	142.4	152.4
3			57.5	57.6	53.4					174.0	110.6	144.9		
4			9.3			726.6	236.15	241.85			219.1	236.2		
5						20.4	16.0	17.4			14.0			
6						36.2								
7						31.4								
R					28.8 38.7		21.65	28.65						

① 化合物 1 ~ 3 在 SbF_5-SO_2ClF-SO_2F_3 中测定；化合物 4 ~ 6 在 SbF_5-SO_2ClF 中测定；化合物 7,8,12 在 SO_2ClF-FSO_3H 中测定；化合物 9 ~ 10 在 FSO_3H-SO_2 中测定；化合物 11 在 FSO_3HSbF_5-SO_2ClF 中测定；化合物 13 ~ 14 在 SbF_5-SO_2ClF 中测定。

1. $n=1$　**2**. $n=2$　**3**. $n=3$

4. R = H　**5**. R = CH_3

6

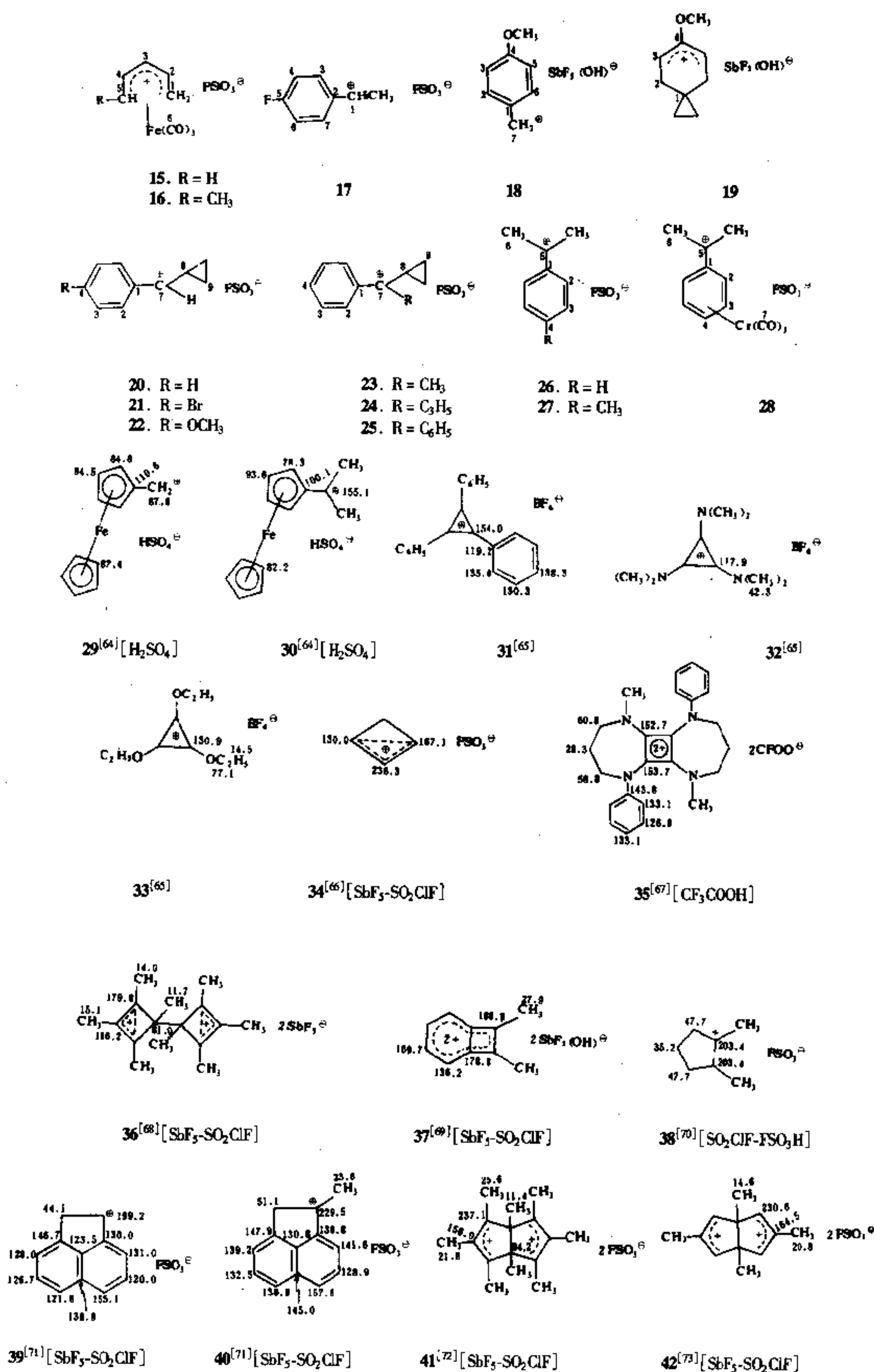
7. $R^1 = OH, R^2 = CH_3$　**8**. $R^1 = CH_3, R^2 = OH$

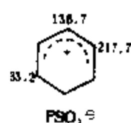
9　**10**　**11**　**12**　**13**. R = H　**14**. R = CH_3

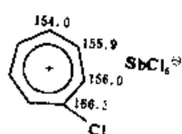
表 19-5　阳碳离子化合物 15 ~ 28 的^{13}C-NMR 化学位移数据[11,60 ~ 63]①

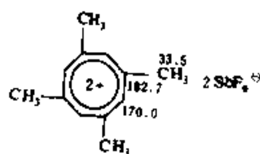
C \ 化合物	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	65.43	62.19	223.4	140.2	48.7	137.8	135.9	132.8	139.8	135.3	141.9 137.3	140.0	137.69	101.66
2	104.62	103.53	138.6	157.0	173.7	145.2	144.9 136.7	150.4 141.4	134.8	129.6	139.0 134.7	142.4	141.52	99.49
3	98.58	94.84	148.6	126.4	122.7	132.2	135.9 135.3	120.6 117.0	131.2	128.0	131.4 129.9	133.3	133.51	120.67
4		104.07	123.1	188.6	169.7	149.0	144.4	179.1	145.5	136.5	150.2 145.2	155.9	174.43	96.72
5		91.31	183.6	119.0								254.3	242.79	170.92
6	197.29 206.02	198.50 207.46	122.1	151.6								34.90	30.90	24.74
7			159.3	168.6		226.3	223.6	208.6	246.2	261.0	235.0			228.39
8						45.1	45.7	30.7	45.8	42.7	40.9			
9						45.1	45.3	29.1	45.0	37.0	35.9			

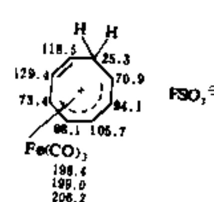
① 化合物 15 ~ 16 在 FSO_3H-SO_2 中测定；化合物 17 在 FSO_3H-SbF_5-SO_2ClF 中测定；化合物 20 ~ 25 在 FSO_3H-SbF_5-SO_2ClF 中测定；化合物 26 ~ 28 在 FSO_3H-SO_2 中测定。


15. R = H
16. R = CH3
17
18
19
20. R = H
21. R = Br
22. R = OCH3
23. R = CH3
24. R = C3H5
25. R = C6H5
26. R = H
27. R = CH3
28
29[64] [H2SO4]
30[64] [H2SO4]
31[65]
32[65]
33[65]
34[66] [SbF5-SO2ClF]
35[67] [CF3COOH]
36[68] [SbF5-SO2ClF]
37[69] [SbF5-SO2ClF]
38[70] [SO2ClF-FSO3H]
39[71] [SbF5-SO2ClF]
40[71] [SbF5-SO2ClF]
41[72] [SbF5-SO2ClF]
42[73] [SbF5-SO2ClF]







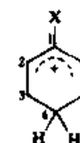


43[66]　　44[74] [CD_3CN]　　45[73] [SbF_5-SO_2ClF]　　46[75] [FSO_3H-SO_2ClF]

表 19-6　阳碳离子化合物 47～60 的^{13}C-NMR 化学位移数据[60,76~79]①

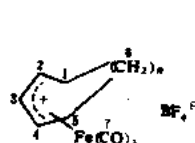
C＼化合物	47	48	49	50	51	52	53	54	55	56	57	58	59	60
1	48.2	48.6	70.7	63.7	183.0	170	63.74	92.58	132.5	132.5	131.7	136.2	133.3	137.4
2	181.1	179.1	170.7	173.7	138	123	101.35	102.60	150.6	148.1	148.4	144.9	143.0	146.0
3	137.5	141.2	137.7	137.7	174	174	89.0	99.43	130.5	129.8	128.8	135.0	133.3	136.8
4	192.0	188.5	159.4	188.7	64	49			150.6	141.2	148.4	143.6	140.9	143.3
5									195.1	218.4	205.2	170.7	190.3	195.3
6							23.07	31.09						
7			59.7	53.7			198.36	198.24						
							208.12	207.89						
10									31.7	35.8	35.4	138.3	134.4	137.8
12									156.6	157.5	158.0	147.1	144.6	146.3
13									137.3	140.0	140.1	142.5	139.5	139.3

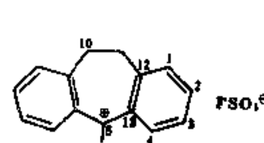
① 化合物 47～48 在 SbF_5-FSO_3H-SO_2ClF 中测定；化合物 49～50 在 SbF_5-SO_2 中测定；化合物 51～52 在 FSO_3HSO_2 中测定；化合物 53～54 在 CH_2Cl_2 中测定；化合物 55～60 在 FSO_3H-SO_2Cl 中测定。



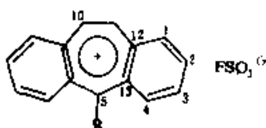


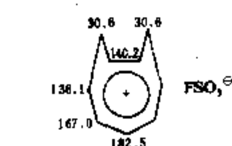


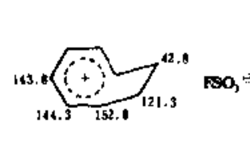


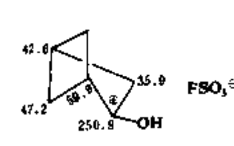


47. X = Cl　　49. R = H　　51. R = CH_3　　53. n = 1　　55. R = H
48. X = Br　　50. R = CH_3　　52. R = OCH_3　　54. n = 2　　56. R = CH_3
57. R = C_6H_5



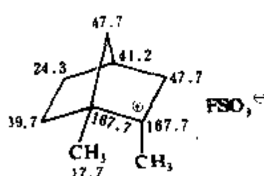


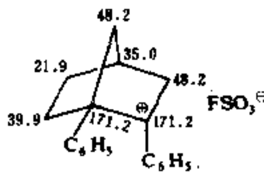


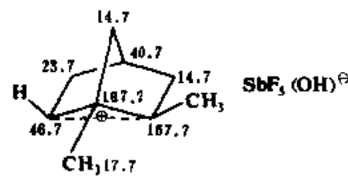


58. R = H
59. R = CH_3
60. R = Cl

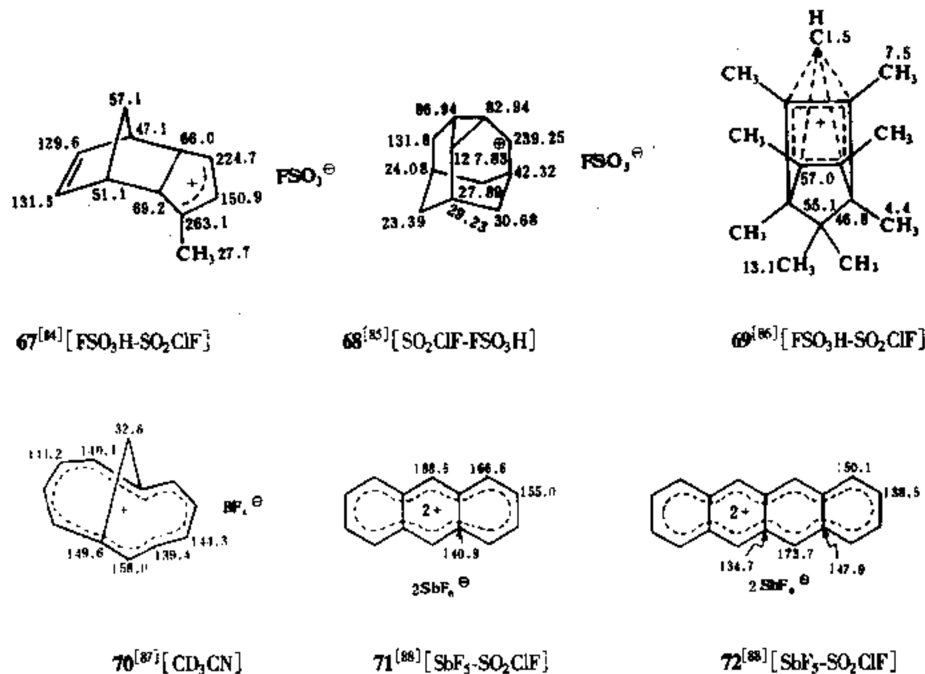
61[80] [FSO_3H-SO_2ClF]　　62[80] [FSO_3H-SO_2ClF]　　63[81] [FSO_3H-SO_2ClF]







64[82] [FSO_3H-SO_2]　　65[82] [FSO_3H-SO_2]　　66[83] [SbF_5-SO_2]



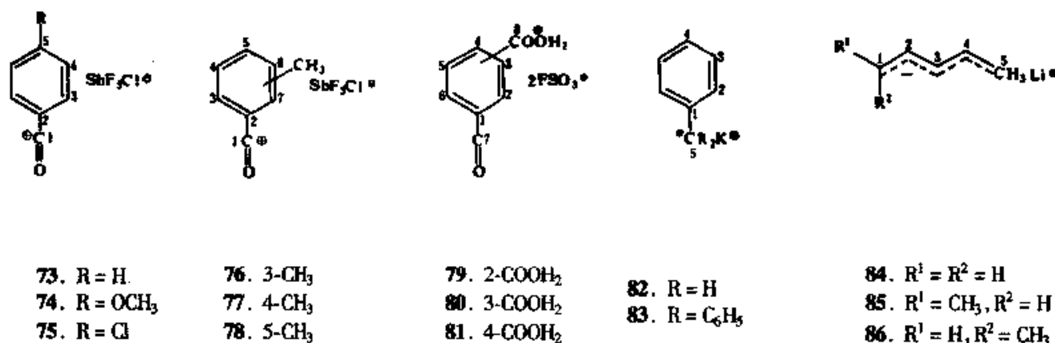
67[84] [FSO_3H-SO_2ClF]　　68[85] [SO_2ClF-FSO_3H]　　69[86] [FSO_3H-SO_2ClF]

70[87] [CD_3CN]　　71[88] [SbF_5-SO_2ClF]　　72[88] [SbF_5-SO_2ClF]

表 19-7　阳碳离子化合物 73～86 的^{13}C-NMR 化学位移数据[89～92]①

C \ 化合物	73	74	75	76	77	78	79	80	81	82	83	84	85	86
1	154.8	161.4	156.1	156.7	157.3	156.5	118.6	92.8	99.4	152.7	148.6	66.2	89.2	85.7
2	87.7	77.1	87.1	88.3	88.0	82.8	134.5	148.2	146.3	110.7	123.5	143.8	139.6	137.3
3	141.3	144.8	145.9	141.2	158.8	140.3		123.7	133.9	130.6	128.8	86.9	83.8	81.4
4	132.9	119.2	138.0	145.9	144.9	133.5		143.4	140.8	95.7	114.2		142.9	143.6
5	149.4	176.4	160.9	152.0	149.9	166.3	140.7	133.2		52.7	88.3		51.5	56.7
6				132.9	131			147.4						
7				140.2	141.3		164.7	158.5	147.2					
8								176.0	178.1					
R		59.8												

① 化合物 73～80 在 SbF_5-SO_2 中测定；化合物 82～83 在四氢呋喃中测定；化合物 84～86 在$(CD_3)_2CO$ 中测定。



73. R = H　　74. R = OCH_3　　75. R = Cl

76. 3-CH_3　　77. 4-CH_3　　78. 5-CH_3

79. 2-$COOH_2$　　80. 3-$COOH_2$　　81. 4-$COOH_2$

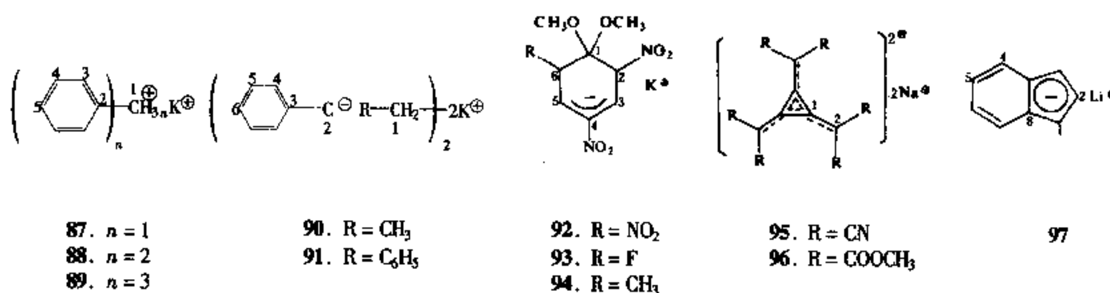
82. R = H　　83. R = C_6H_5

84. $R^1 = R^2 = H$　　85. $R^1 = CH_3, R^2 = H$　　86. $R^1 = H, R^2 = CH_3$

表 19-8　阳碳离子化合物 87～97 的^{13}C-NMR 化学位移数据[93～97]①

C \ 化合物	87	88	89	90	91	92	93	94	95	96	97
1	52.8	79.1	88.2	137.5	145.8	104.3	103.7	106.0	124.5	138.4	91.8
2	153.2	145.9	148.9	103.3	117.5	129.2	121.2	120.7	24.8	72.7	114.5
3	111.0	117.0	123.9	129.6	129.3	131.2	128.8	130.9			
4	130.8	129.4	128.9	88.0	108.1	119.3	118.4	122.6			120.6
5	95.6	108.2	114.4	78.4	86.9	131.2	107.8	123.9			116.4
6				33.7	30.5	129.2	148.3	125.4			
7											
8											127.5
R				19.2					121.0	169.3 49.3	

① 化合物 87～91 在四氢呋喃中测定；化合物 92～94 在$(CD_3)_2SO$ 中测定；化合物 95～96 在 $CH_3OCH_2CH_2OCH_3$ 中测定；化合物 97 在$(C_2H_5)_2O$ 中测定。



87. $n=1$　**88**. $n=2$　**89**. $n=3$

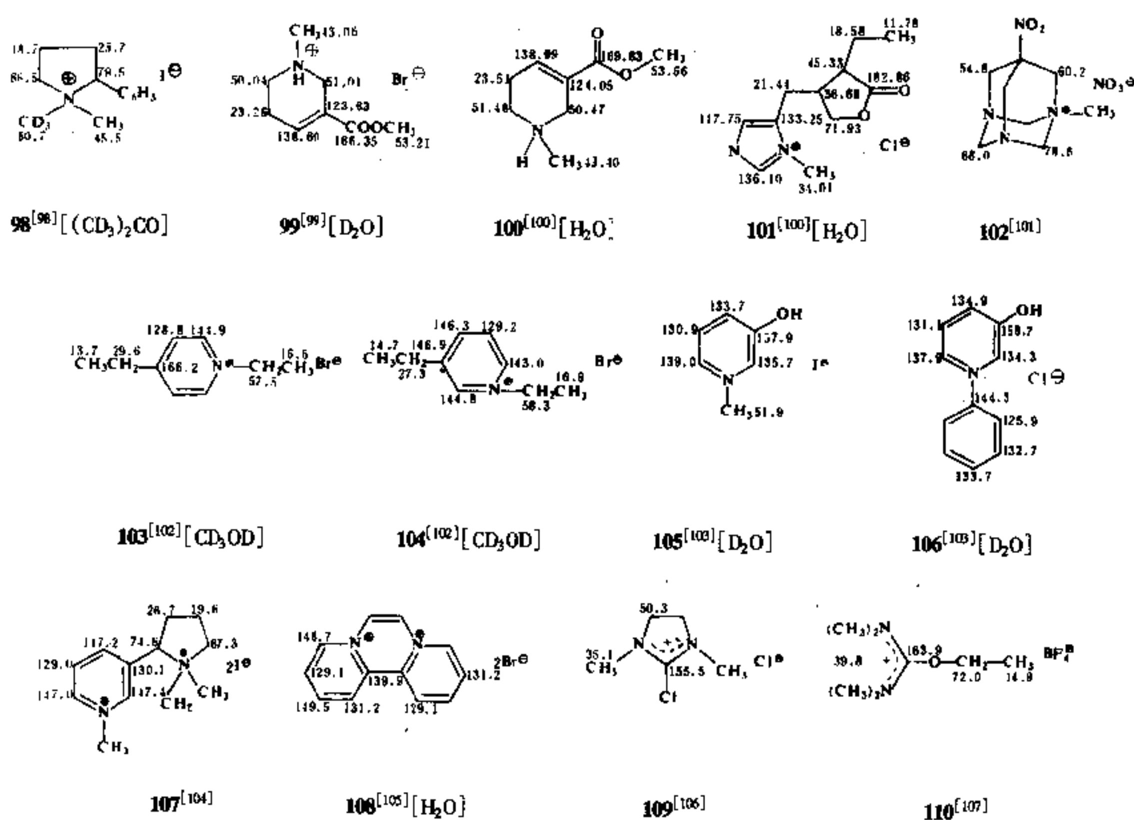
90. R = CH_3　**91**. R = C_6H_5

92. R = NO_2　**93**. R = F　**94**. R = CH_3

95. R = CN　**96**. R = $COOCH_3$

97

二、杂离子化合物的^{13}C-NMR 化学位移



98[98][$(CD_3)_2CO$]　**99**[99][D_2O]　**100**[100][H_2O]　**101**[100][H_2O]　**102**[101]

103[102][CD_3OD]　**104**[102][CD_3OD]　**105**[103][D_2O]　**106**[103][D_2O]

107[104]　**108**[105][H_2O]　**109**[106]　**110**[107]

111[107]　　112[107]　　113[107]　　114[107]

115[108]　　116[109] [$CH_3COOH + CDCl_3$]　　117[109] [$CH_3COOH + CDCl_3$]

118[110] [DCOOD]　　119[110] [DCOOD]　　120[111]

表 19-9　杂离子化合物 121～133 的^{13}C-NMR 化学位移数据[112～117]①

C \ 化合物	121	122	123	124	125	126	127	128	129	130	131	132	133
1			65.0	63.9	66.3			167.7	154.3				
2	44.85	45.56	27.2	35.3	36.6	142.52	146.47			145.8	146.0	163.66	156.67
3	22.50	22.24	18.4	59.4	63.2	128.72	129.21	42.9	54.1	128.9	134.2	126.69	129.93
4	30.09	30.71				148.42	146.47	25.0	27.1	146.2	148.2	162.24	160.98
5	32.12	32.85						138.6	134.9		129.0	19.47	22.26
6	24.94	19.09		26.9	26.8			123.6	129.5		144.6	22.14	21.97
7	24.84	31.85		13.0	18.2			139.7	138.0				
8	29.87	30.19						130.0	129.5				
9	61.29	64.29		52.8	52.6			135.5	133.6				
10	39.11	32.49		53.4	53.5			124.7	123.8				
R													40.61

① 化合物 123～125,130～131 在 D_2O 中测定;化合物 128～129 在 D_2O/DCl 中测定;化合物 132～133 在 CF_3COOH/CD_2Cl_2 中测定。

121. R = H
122. R = CH_3

123. $R^1 = R^2 = H$
124. $R^1 = H, R^2 = OH$
125. $R^1 = OH, R^2 = H$

126. R = H, X = HSO_4
127. R = CH_3, X = FSO_3

128. R = D
129. R = OH

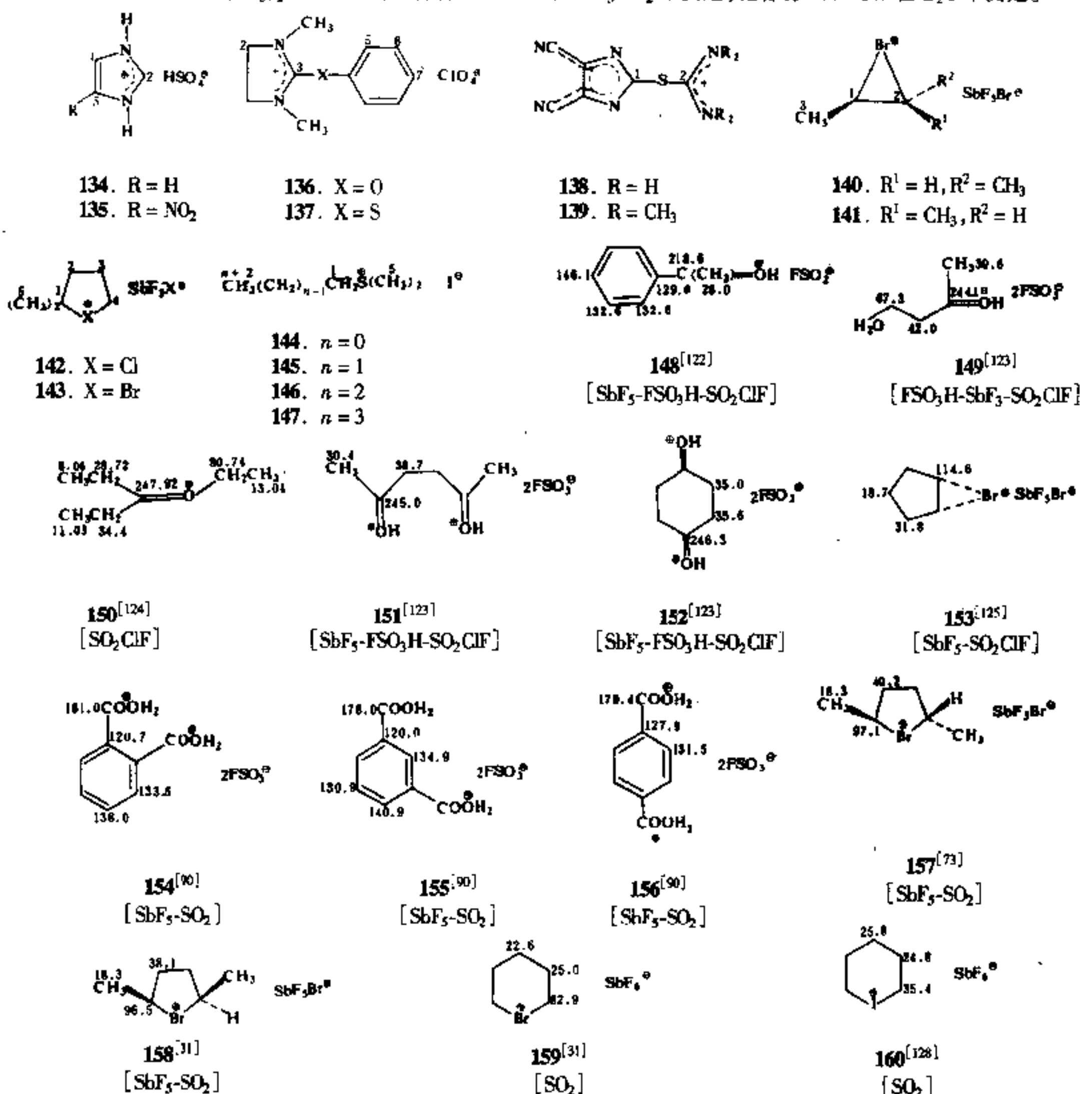
130. R = H
131. R = $CONH_2$

132. R = H
133. R = CH_3

表 19-10　杂离子化合物 134～147 的 ^{13}C-NMR 化学位移数据[107,118～121]①

C \ 化合物	134	135	136	137	138	139	140	141	142	143	144	145	146	147
1			33.1	35.4	142.17	144.57	110.2	107.8	195.1	151.0	27.5	38.2	45.4	43.2
2	134.1	136.4	48.0	50.9	168.29	172.19			48.9	50.1		8.3	17.7	25.7
3			158.9	164.3			21.4	16.4	37.0	37.7			12.7	21.4
4	119.7	139.3	152.2	124.7					66.2	66.1				13.7
5	119.7	121.0	118.6	131.9					35.2	33.8		24.3	24.8	25.3
6			130.6	130.2										
7			126.8	129.7										
8														

① 化合物 138～139 在 $(CD_3)_2SO$ 中测定；化合物 140～143 在 SbF_5-SO_2 中测定；化合物 144～147 在 D_2O 中测定。



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103 Takeuchi Y et al. Org Magn Reson, 1976; 8: 21
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107 Kalinowski H-O et al. Org Magn Reson, 1975; 7: 128
108 Holm A et al. J Org Chem, 1975; 40: 431
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112 E leil E L et al. J Org Chem, 1976; 41: 199
113 Wiseman J R et al. J Org Chem, 1975; 40: 3222
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115 Christl M, Org Magn Reson, 1975; 7: 349
116 Lepoivre J A et al. Org Magn Reson, 1975; 7: 422
117 Balaban A T et al. Org Magn Reson, 1977; 9: 16
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122 Olah G A et al. J Am Chem Soc, 1974; 96: 3548
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124 Olah G A et al. J Am Chem Soc, 1976; 98: 2245
125 Olah G A et al. J Am Chem Soc, 1976; 98: 8113

第二十章　生物碱的^{13}C-NMR化学位移

生物碱的^{13}C-NMR谱化学位移具有如下一些特征。

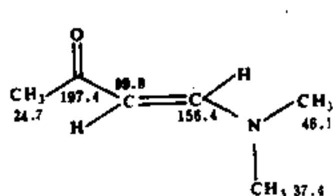
① 由于生物碱结构中氮原子的电负性影响，使 α 碳明显向低场位移。在芳氮杂环中，氮使 α 碳向低场位移最大，γ 碳次之，而 β 碳位移最小；在脂氮杂环中，氮原子对 α 碳影响最大。

② 季铵盐中氮原子使 α 碳向更低场位移，氮氧化物和季铵中的氮也使 α 碳向低场位移。

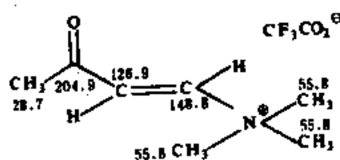
③ 很多生物碱分子中含有氮甲基，由于氮的电负性使甲基碳在较低场出现。

④ 生物碱的构型和构象不同，化学位移也是不同的，e 键甲基使 α、β 碳去屏蔽，因此使 α、β 碳向低场位移，对 γ 碳影响不大；a 键使 α、β 碳向低场位移，而使 γ 碳向高场位移。

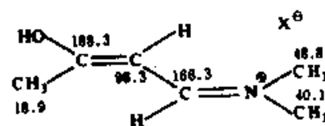
第一节　有机胺类生物碱的^{13}C-NMR化学位移



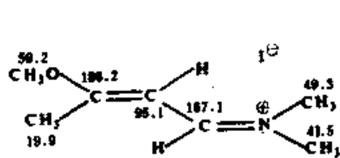
1[1][CHCl$_2$F]



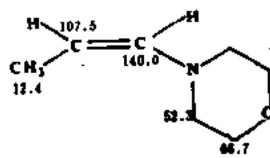
2[1][三氟乙酸]



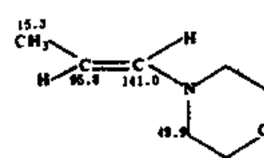
3[1][三氟乙酸]



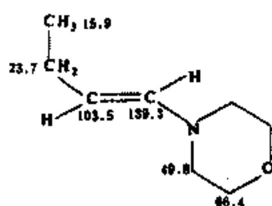
4[1][CD$_3$OD]



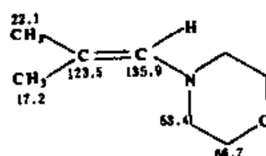
5[2][纯物质]



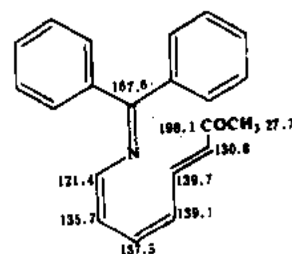
6[2][纯物质]



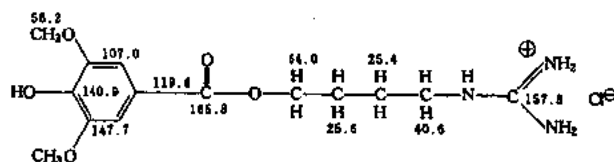
7[2][纯物质]



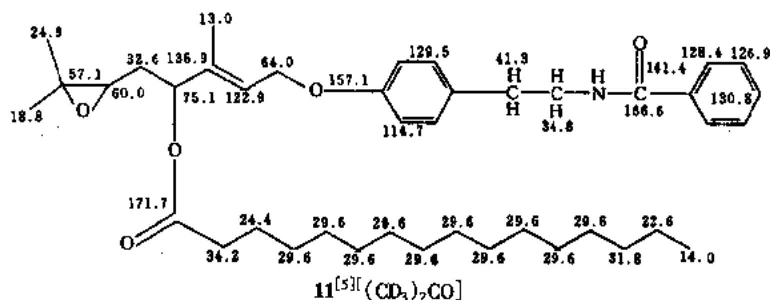
8[2][纯物质]



9[3]



10[4][(CD$_3$)$_2$SO]

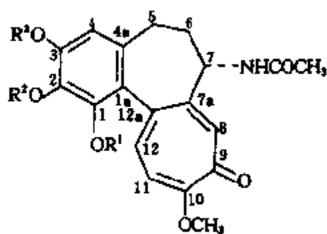


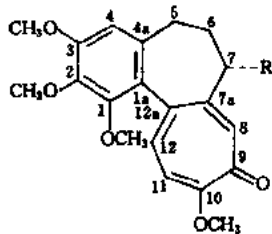
11[5][$(CD_3)_2CO$]

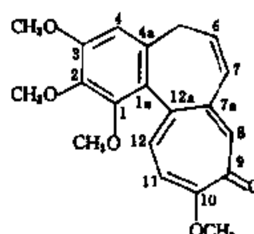
表 20-1　秋水仙碱 12～19 的^{13}C-NMR 化学位移数据[6～7]

C ＼ 化合物	12	13①	14	15	16	17	18	19
1	152.9	150.8	142.1	150.6	150.6	151.4	150.9	151.8
2	134.5	135.9	140.1	141.6	141.6	142.2	141.6	141.7
3	153.6	147.0	153.8	153.5	153.4	153.6	153.6	152.9
4	107.5	103.3	110.0	107.5	107.5	107.6	107.4	107.1
5	36.2	29.5	30.1	30.4	30.6	30.0	30.7	39.0
6	30.0		37.1	38.7	36.3	34.0	40.6	130.5
7	52.9	50.8	52.2	62.8	68.5	57.2	53.8	129.7
8	130.5	130.7	131.3	132.3	134.2	130.9	132.0	133.7
9	179.6	178.0	179.7	179.8	180.1	179.5	179.8	178.5
10	164.1	163.3	164.4	164.1	164.1	164.2	164.0	164.1
11	113.2	112.3	112.3	111.9	111.7	112.0	111.9	111.4
12	135.8	135.5	134.0	134.6	133.8	133.9	135.3	136.1
1a	125.7	119.4	125.7	126.0	125.9	126.4	125.9	128.2
4a	151.1	134.4	134.4	135.3	134.8	133.9	134.5	133.1
7a	137.2	152.2	151.8	150.9	152.0	151.4	154.5	154.1
12a	141.6	134.0	136.3	137.2	137.5	136.2	136.5	135.4
1—OCH_3	56.4		60.8	60.8	60.6	61.3	61.0	61.1
2—OCH_3	61.3	60.2	60.4	61.2	61.2	61.6	61.1	61.3
3—OCH_3	56.4	55.7	56.5	56.2	56.1	56.2	56.3	56.1
10—OCH_3	56.1	55.9	56.3	56.2	56.1	56.3	56.3	56.2
—NCO—	170.3	168.2	169.3			171.1		
$NCOCH_3$	22.6	22.5	22.9			22.4		
> N—CH_3				34.5	43.7	33.8		
—OCO—			169.8					
—$OCOCH_3$			20.0					

① 化合物 13 在$(CD_3)_2SO$ 中测定。







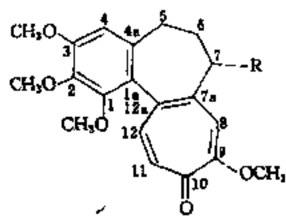
12. $R^1 = R^2 = R^3 = CH_3$
13. $R^2 = R^3 = CH_3, R^1 = H$
14. $R^2 = R^3 = CH_3, R^1 = COCH_3$

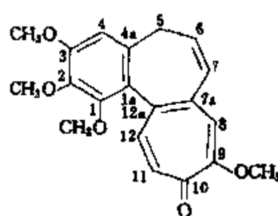
15. R = $NHCH_3$
16. R = $N(CH_3)_2$
17. R = NCH_3COCH_3
18. R = NH_2

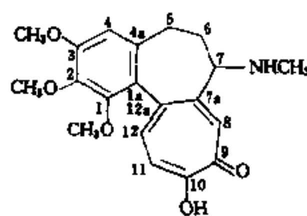
19

表 20-2 秋水仙碱 20～26 的^{13}C-NMR 化学位移数据[7]

C \ 化合物	20	21	22	23	24	25	26
1	151.2	150.7	151.5	150.9	150.6	151.5	150.6
2	142.1	141.1	141.6	141.8	141.8	141.4	141.6
3	154.2	153.6	153.7	153.9	153.7	152.9	153.7
4	108.0	107.5	107.6	107.6	107.4	106.8	107.7
5	30.1	30.4	30.7	30.1	30.7	38.6	30.3
6	37.6	40.1	37.7	36.5	42.4	131.0	39.8
7	53.7	63.0	68.9	58.9	53.0	129.6	39.8
8	110.4	111.2	112.4	109.4	111.1	115.9	118.3
9	164.1	164.1	163.9	164.0	163.9	162.8	173.0
10	179.5	179.6	179.8	179.4	179.6	179.4	168.2
11	133.9	133.8	133.8	134.0	133.6	132.0	124.5
12	141.8	141.4	140.7	141.0	141.3	142.1	141.8
1a	125.9	126.0	126.2	125.6	125.9	128.4	126.3
4a	134.8	135.7	135.4	134.7	135.9	133.2	135.5
7a	143.1	145.4	146.1	143.6	147.2	144.4	151.3
12a	135.4	135.2	135.4	134.3	134.2	132.6	136.5
CH_3O—1	61.1	61.0	60.6	61.2	60.9	61.0	61.0
CH_3O—2	61.4	61.2	61.3	61.4	61.1	61.3	61.2
CH_3O—3	56.1	56.1	56.1	55.8	56.2	51.6	56.2
CH_3O—10	56.3	56.1	56.1	56.2	56.2	56.1	
—NCO—	157.5			171.5			
—NCOC ←	116.4			22.2			
N—CH_3		35.2	44.2	36.5			35.0





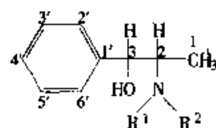


20. R = $NHCOCF_3$
21. R = $NHCH_3$
22. R = $N(CH_3)_2$
23. R = NCH_3COCH_3
24. R = NH_2

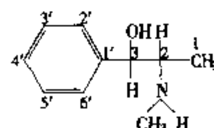
25　　26

表 20-3 麻黄生物碱 27～30 的^{13}C-NMR 化学位移数据[8]

C \ 化合物	27	28	29	30	C \ 化合物	27	28	29	30
C—1	10.6	12.8	8.5	13.3	C—1′	139.4	140.5	140.3	139.4
C—2	60.8	60.5	67.4	53.3	C—2′,6′	126.9	127.8	126.8	127.1
C—3	72.1	75.5	71.5	73.7	C—3′,5′	129.6	129.8	129.8	129.7
N—Me	31.7	30.9	41.1		C—4′	129.2	129.8	129.3	129.4
Me			42.8						



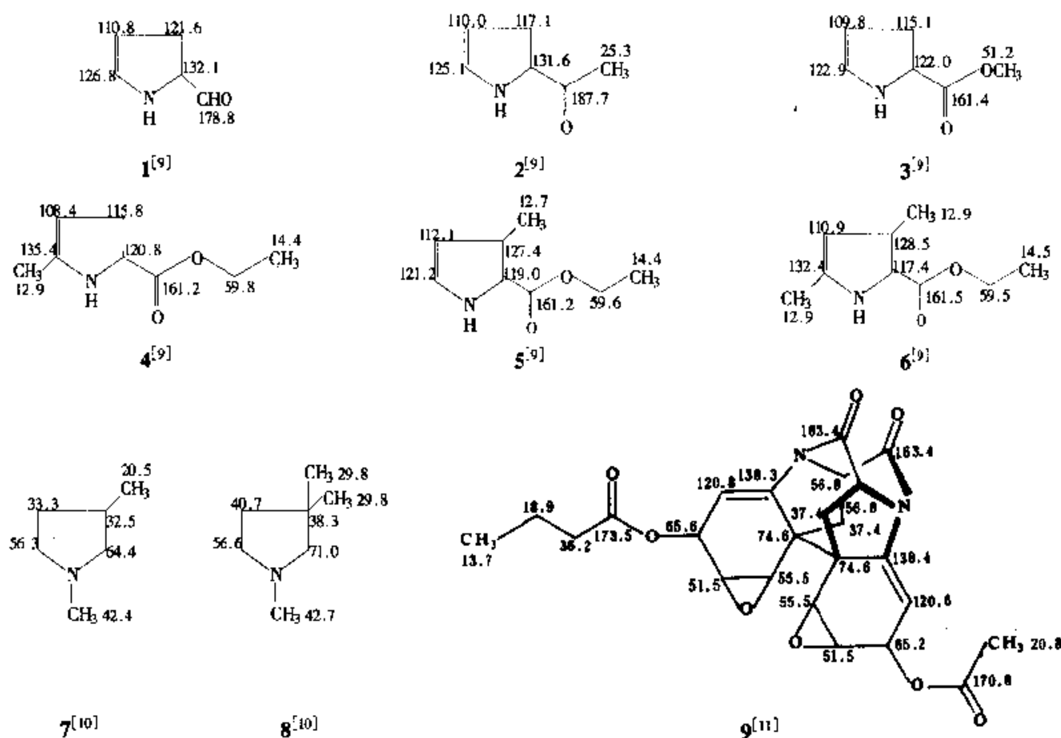
27. R^1 = H, R^2 = Me
28. R^1 = R^2 = Me
29. R^1 = R^2 = H



30

第二节　吡咯及吡咯里西啶类生物碱的^{13}C-NMR 化学位移

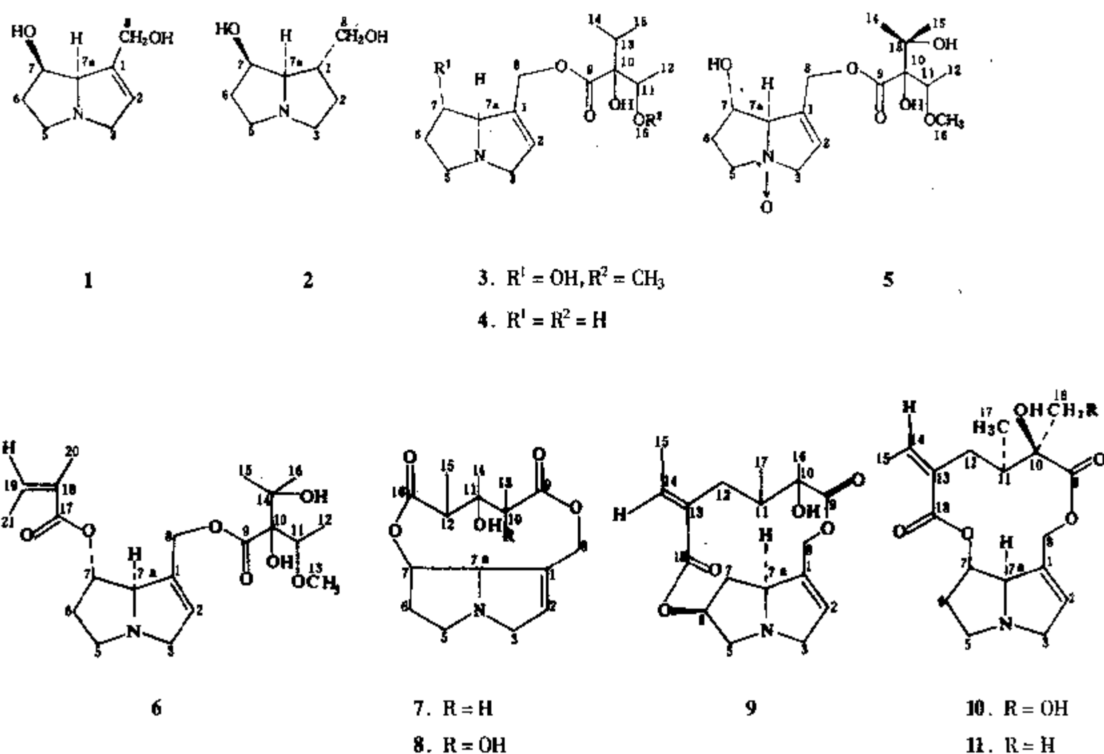
一、吡咯类生物碱的^{13}C-NMR 化学位移



二、吡咯里西啶生物碱的^{13}C-NMR 化学位移

表 20-4　吡咯里西啶生物碱 1～11 的^{13}C-NMR 化学位移数据[12～14]

C ＼ 化合物	1	2	3	4	5	6	7	8	9	10	11
1	137.9	45.8	136.4	137.9	132.2	135.0	132.9	132.8	129.9	132.4	131.7
2	127.1	30.4	127.4	125.6	124.4	128.6	135.5	134.3	136.1	134.7	135.9
3	58.7	57.2	62.0	61.9	68.6	62.3	60.9	60.4	59.3	61.0	59.9
5	54.2	55.6	54.2	56.9	61.9	54.3	53.2	53.7	66.4	52.9	52.9
6	35.3	38.3	34.3	25.9	33.6	30.5	33.6	33.5	74.7	37.9	34.6
7	71.1	75.0	75.6	30.2	97.1	76.9	76.3	76.7	73.7	77.4	77.5
7a	79.5	73.1	78.6	69.3	72.3	78.9	75.3	75.0	75.2	75.0	74.7
8	61.9	63.4	62.8	62.4	77.9	62.3	61.3	61.3	61.5	62.7	62.7
9	-		175.1	175.2	174.4	173.9	175.6	173.5	176.9	175.7	177.3
10			82.6	83.1	86.1	83.8	37.6	78.7	76.3	81.3	76.6
11			80.1	71.5	79.7	78.9	76.3	76.8	40.5	35.7	37.3
12			12.5	17.3	13.5	13.0	48.1	44.2	27.6	34.7	38.3
13			31.8	33.1	74.3	56.5	27.1	22.0	135.6	131.2	133.2
14			17.1	17.1	26.4	73.0	18.4	17.7	142.5	136.6	133.7
15			16.4	17.0	25.7	24.6	11.3	13.6	15.0	14.9	14.9
16			57.0		57.1	26.5	174.4	174.1	24.6	66.9	24.9
17						167.8			10.8	11.6	10.9
18						127.7			167.0	167.3	167.4
19						138.5					
20						20.5					
21						15.9					

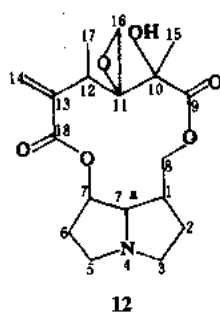


1　2　3. $R^1 = OH, R^2 = CH_3$　4. $R^1 = R^2 = H$　5

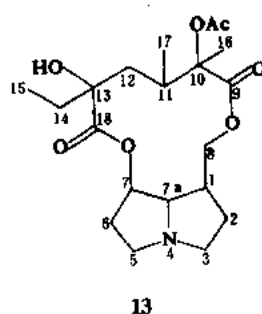
6　7. R = H　8. R = OH　9　10. R = OH　11. R = H

表 20-5　吡咯里西啶生物碱 12～14 的 ^{13}C-NMR 化学位移数据

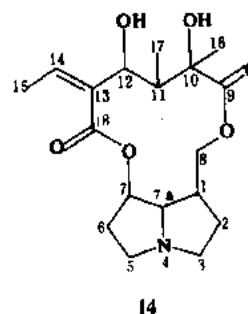
C ＼ 化合物	12	13	14	C ＼ 化合物	12	13	14
1	131.8	131.6	41.9	10	77.4	83.6	78.1
2	136.6	135.7	29.8	11	79.4	37.3	40.7
3	61.2	60.6	54.4	12	35.6	39.6	70.0
5	53.1	53.2	52.2	13	143.1	78.8	133.5
6	34.1	34.6	35.3	14	122.0	33.3	135.1
7	75.9	76.9	73.5	15	21.9	7.4	15.6
7a	77.6	77.5	75.4	16	41.7	14.9	25.7
8	62.6	63.3	65.2	17	16.9	15.9	5.9
9	176.6	176.1	178.2	18	168.1	172.1	167.6



12

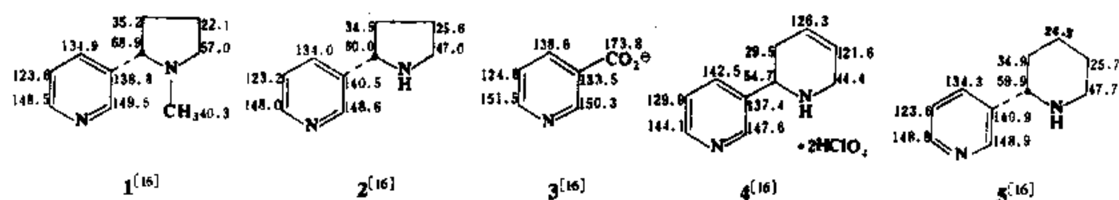


13

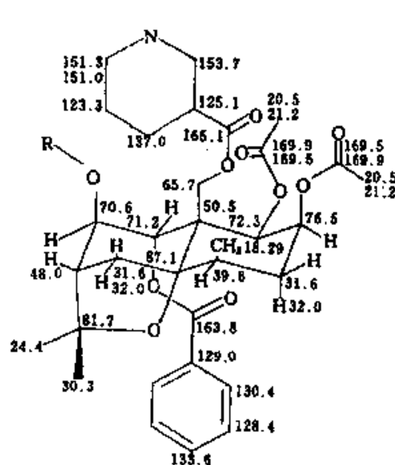


14

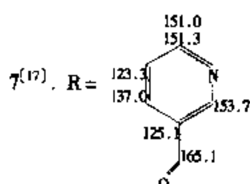
第三节 吡啶及六氢吡啶类生物碱的^{13}C-NMR 化学位移



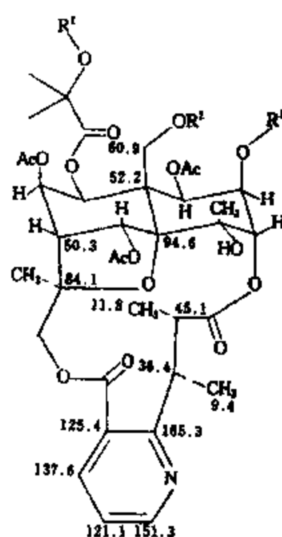
1[16]　　2[16]　　3[16]　　4[16]　　5[16]



6[17]. R = H



7[17]. R =

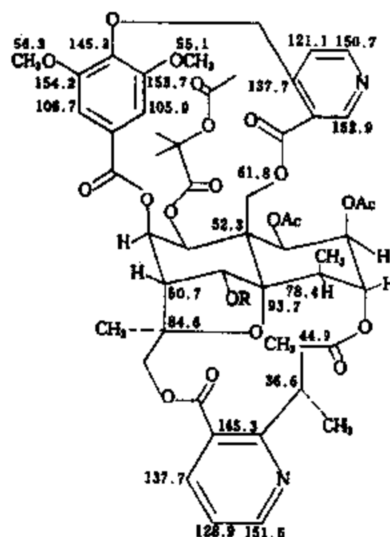


8[17]. $R^1 = R^2 = R^3 = Ac$

9[17]. $R^1 = R^2 = Ac, R^3 = H$

10[17]. $R^1 = Ac, R^2 = R^3 = H$

11[17]. $R^1 = R^2 = R^3 = H$



12[17]. R = H

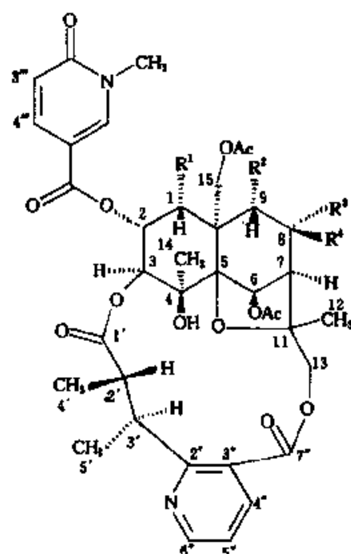
13[17]. R = Ac

表 20-6　倍半萜生物碱 14～22 的^{13}C-NMR 谱化学位移数据[166,167]

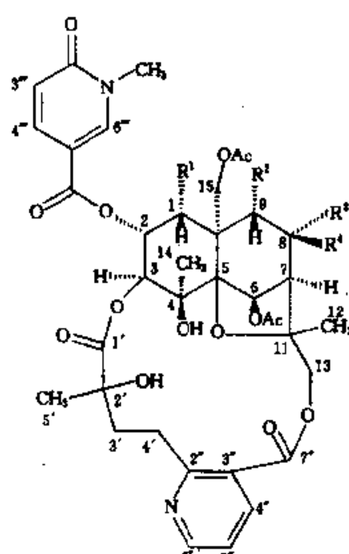
C \ 化合物	14	15	16	17	18	19	20	21	22
1	70.8	72.5	74.5	73.5	73.1	73.2	73.1	73.2	73.2
2	69.6	72.1	70.5	68.7	69.4	68.7	68.7	69.0	68.7
3	75.4	75.6	75.2	76.6	75.7	75.7	75.6	75.6	75.8
4	70.5	69.9	70.2	69.2	70.5	70.6	70.6	70.7	70.6
5	93.7	93.8	93.8	94.2	94.1	93.7	94.0	94.0	93.7
6	73.6	73.7	74.5	70.4	73.8	73.9	74.2	74.2	74.8
7	50.2	50.5	49.3	51.2	50.7	50.3	50.5	50.4	50.4
8	71.3	69.3	74.5	70.4	69.0	68.9	68.8	69.0	69.1
9	71.8	71.2	76.3	69.9	70.6	70.6	70.2	70.6	70.8
10	54.0	52.2	51.2	52.1	52.2	52.1	52.7	52.6	52.2
11	84.8	84.0	85.5	84.8	84.4	84.1	84.3	84.4	84.2
12	18.3	18.5	19.3	17.9	18.7	18.5	18.6	18.6	18.4
13	70.1	70.2	70.2	70.7	70.0	69.8	69.8	69.9	69.9
14	23.7	23.3	24.3	22.8	23.4	22.9	23.8	24.1	22.9

续表

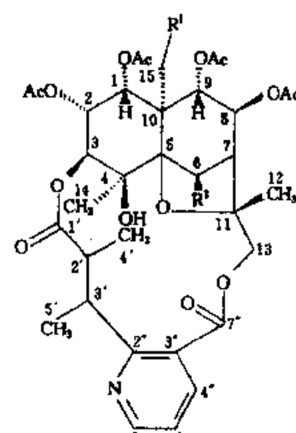
C \ 化合物	14	15	16	17	18	19	20	21	22
15	60.4	60.7	60.5	60.2	60.5	60.0	60.0	61.0	60.0
1′	173.9	173.8	173.8	172.3	174.0	173.9	174.0	174.0	173.9
2′	44.7	45.1	44.8	77.9	45.1	44.9	44.9	44.9	45.0
3′	36.7	36.6	36.6	38.4	36.5	36.4	36.3	36.4	36.3
4′	9.8	9.9	10.0	30.9	9.9	9.5	9.7	9.7	9.6
5′	12.2	12.1	12.4	28.3	12.0	11.8	11.8	11.9	11.8
2″	165.1	165.1	165.1	165.0	165.7	165.0	165.4	165.4	165.2
3″	125.2	125.1	125.2	126.0	125.1	125.2	125.0	125.0	125.1
4″	138.6	137.7	137.6	137.8	138.0	137.5	137.7	137.7	137.7
5″	121.5	121.1	121.1	122.0	121.3	121.1	121.1	121.1	121.1
6″	151.4	151.5	151.5	147.4	151.7	151.5	151.5	151.5	151.5
7″	162.8	162.9	163.0	162.6	162.7	169.1	168.7	168.5	169.0
2‴	163.0	163.6	163.6	162.9	163.2				
3‴	119.9	119.9	119.8	119.9	120.0				
4	139.0	139.0	138.8	138.7	139.1				
5	108.1	108.3	108.2	107.8	108.4				
5	144.0	144.2	144.1	144.3	144.2				
7‴	168.5	168.5	168.3	167.7	168.6	161.8	162.2	166.0	165.8
C_1-	20.8			20.6	20.6	20.5	20.5	20.4	20.5
OAc	170.4			172.3	169.0	169.0	169.3	169.5	169.1
C_2-						21.0	21.1	21.1	21.1
OAc						168.0	168.5	168.5	168.5
C_6-	21.3	20.8	21.0	20.7	20.7		21.7	21.7	
OAc	170.0	169.9	169.7	169.3	170.2		170.0	169.7	
C_8-	21.3	21.3	21.3	21.3	21.2	21.0	20.4	20.6	21.0
OAc	170.4	170.8	170.5	170.9	170.3	170.2	170.3	170.0	170.2
C_9-		21.1		21.5	21.5	20.4	20.3	20.2	20.4
OAc		162.7		168.9	162.7	168.8	169.0	169.0	168.6
C_{15}-	21.7	21.6	21.7	21.8	21.8	21.4			21.4
OAc	170.9	170.0	170.8	169.8	171.2	170.1			170.2
N-CH_3	38.3	38.2	38.3	38.4	38.3				



14. $R^1 = R^3 = OAc, R^2 = OH, R^4 = H$
15. $R^1 = OH, R^2 = R^3 = OAc, R^4 = H$
16. $R^1 = R^2 = OH, R^3 = H, R^4 = OAc$
18. $R^1 = R^2 = R^3 = OAc, R^4 = H$



17. $R^1 = R^2 = R^3 = OAc, R^4 = H$

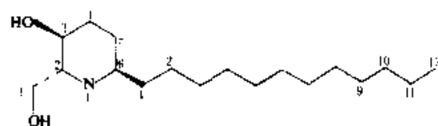


19. $R^1 = OAc, R^2 = OFu$
20. $R^1 = OFu, R^2 = OAc$
21. $R^1 = OBz, R^2 = OAc$
22. $R^1 = OAc, R^2 = OBz$

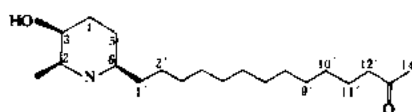
表 20-7　六氢吡啶生物碱 23～27 的^{13}C-NMR 化学位移数据[18]①

C＼化合物	23	24	25	26	27	C＼化合物	23	24	25	26	27
2	57.9	57.7	57.7	57.6	55.4	5′	29.3	23.7	29.2	29.2	29.4
3	67.9	67.9	67.9	67.5(c)	67.7	6′	29.3	42.5	23.7	29.2	29.4
4	27.2	27.2	27.2	26.0	32.0	7′	29.3	(d)	42.5	29.2	29.4
5	28.4	28.4	28.4	27.5	26.1(c)	8′	23.9	42.5	(d)	29.2	29.4
6	50.0	50.0	50.0	50.4	57.0	9′	42.3	23.7	42.5	25.4	29.4
1″	62.2	62.3	62.3	61.4	18.7	10′	(d)	31.3	26.2	38.8	29.4
1′	33.3	32.5	32.5	31.8	37.0	11′	35.7	22.2	22.2	67.0(c)	23.7
2′	26.3	26.2	26.2	26.0	25.7(c)	12′	7.9	13.7	13.7	27.7	43.8
3′	29.3	29.2	29.2	29.2	29.4	13′					(d)
4′	29.3	29.2	29.2	29.2	29.4	14′					29.4

① 化合物 18 在 $CDCl_3+CH_3OH$ 体积比为 2:1 中测定；(c)彼此之间可互换数据；(d)表示未观测。

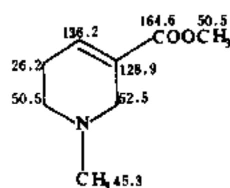


23. 10′ = O
24. 7′ = O
25. 8′ = O
26. 11′ = OH

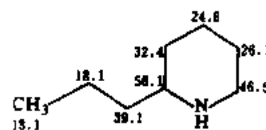


27

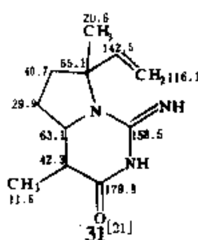
28[19]



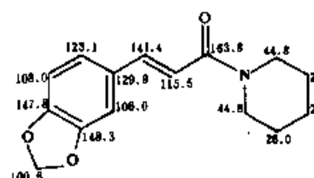
29[20]



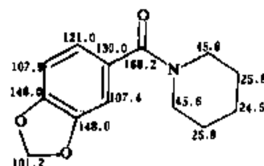
30[20]



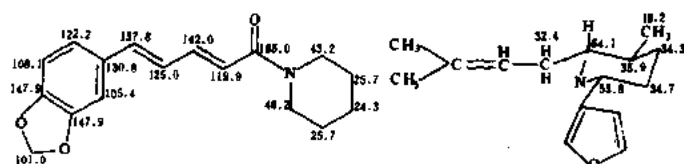
31[21]



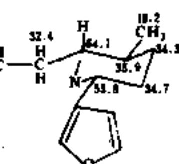
32[22]



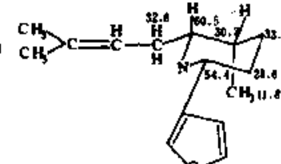
33[22]



34[22]



35[23]



36[23]

第四节　莨菪烷类与吖啶酮类生物碱的¹³C-NMR化学位移

一、莨菪烷类生物碱的¹³C-NMR化学位移

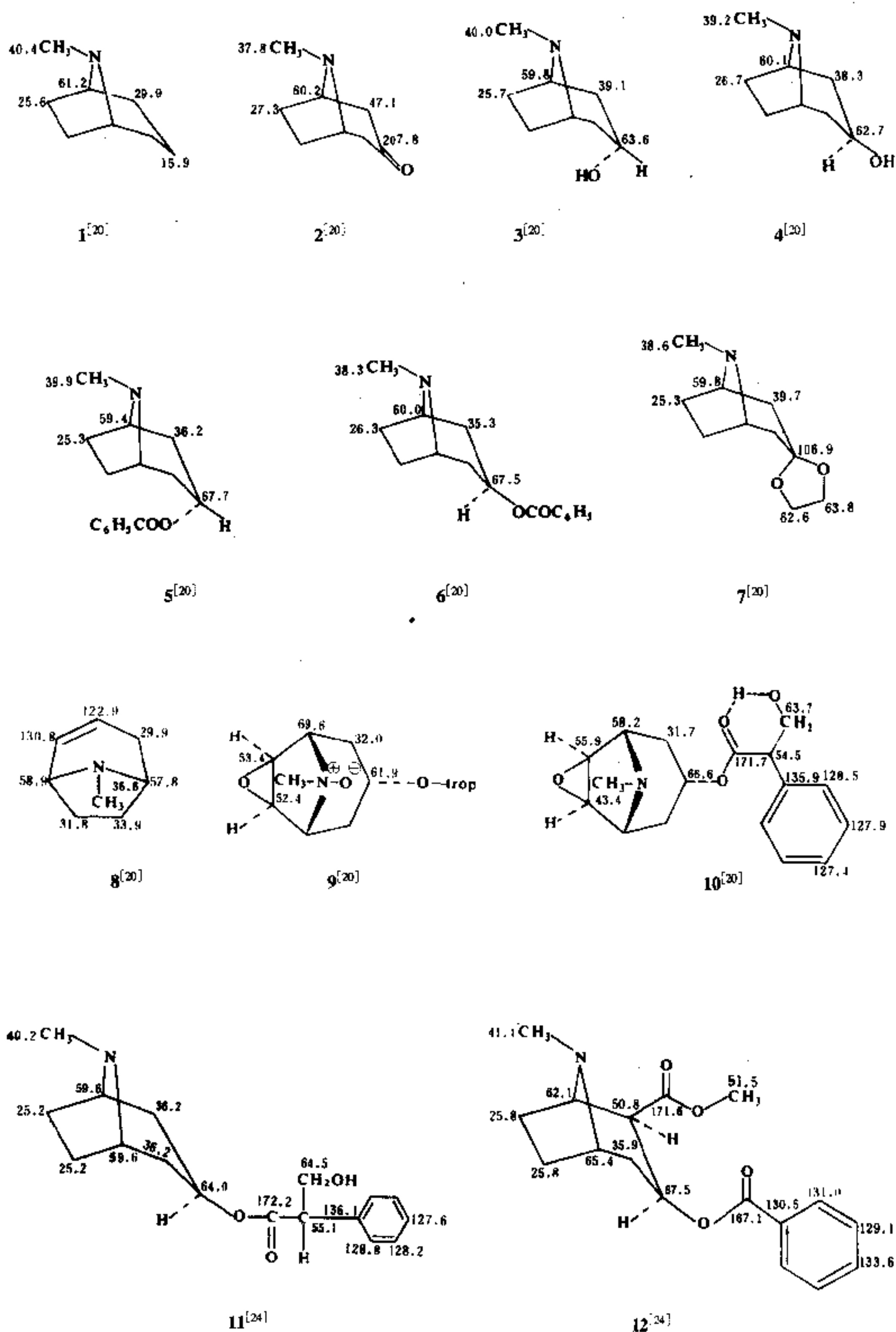
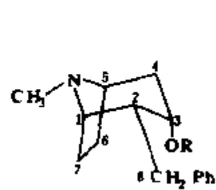
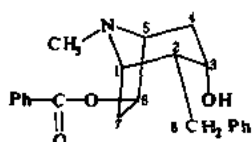


表 20-8　2-苄基莨菪烷 13～19 的^{13}C-NMR 化学位移数据[25]

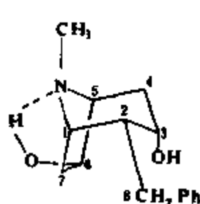
C \ 化合物	13	14	15	16	17	18	19
1	63.2	63.2	63.3	64.2	62.8	70.7	62.5
2	45.8	45.8	45.4	44.9	40.0	38.6	49.4
3	69.7	69.7	69.3	65.4	66.0	69.3	64.6
4	37.0	37.0	37.0	36.9	32.7	31.0	36.0
5	59.5	59.6	59.8	66.5	67.4	58.3	66.3
6	25.3	25.3	25.3	80.5	76.2	40.9	80.3
7	21.9	21.9	21.6	32.2	37.1	72.8	33.1
8	35.2	35.2	35.1	35.2	35.1	35.0	74.2
9	139.0	139.0	139.2	140.0	139.8	138.9	142.7
10	127.9	127.9	128.1	128.1	128.3	127.9	126.4
11	128.7	128.7	128.7	128.8	128.7	128.7	128.4
12	125.7	125.7	125.8	125.7	125.8	126.0	127.8
1′		130.3		130.3			130.3
2′		129.2		129.2			129.2
3′		128.1		128.1			128.1
4′		132.7		132.7			132.7
C＝0		165.8		165.8			165.8
N-CH_3	40.3	40.3	40.4	40.6	36.8	36.7	40.3



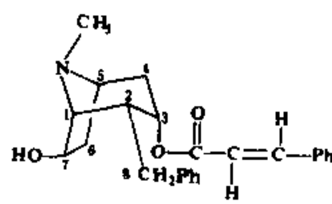
13. R＝H
14. R＝COPh
15. R＝$COCH_3$



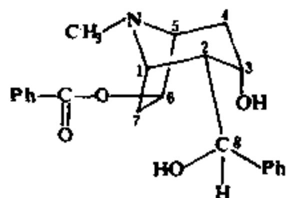
16



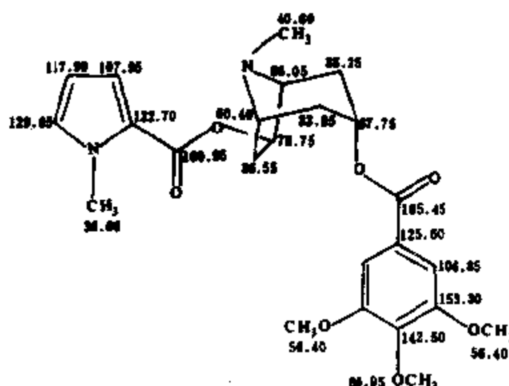
17



18



19



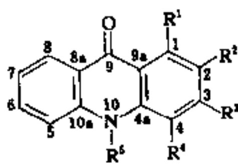
20[26]

二、吖啶酮类生物碱的13C-NMR化学位移

表 20-9 吖啶酮类生物碱 1～8 的13C-NMR 化学位移数据[27]①

C＼化合物	1	2	3	4	5	6	7	8
1	126.0	127.3	101.9	102.6	162.6	137.3	138.3	141.8
2	120.5	121.5	144.4	143.4	90.4	133.7	134.8	132.7
3	133.4	134.2	152.6	153.4	163.8	141.8	145.1	154.6
4	117.3	115.2	95.7	95.9	92.3	126.2	128.9	90.1
5	117.3	115.2	117.0	116.0	114.7	117.5	115.6	115.0
6	133.4	134.2	132.5	133.1	132.5	133.2	132.6	133.4
7	120.5	121.5	120.9	121.1	120.8	122.2	121.3	121.8
8	126.0	127.3	127.5	126.3	126.7	126.5	126.7	127.3
9	176.8	178.7	175.8	174.8	175.6	178.3	177.4	177.8
4a	140.8	142.6	139.2	140.3	146.6	134.7	137.1	143.2
8a	120.5	122.1	120.7	121.1	124.1	122.2	124.3	123.7
9a	120.5	122.1	115.2	116.7	107.8	110.8	114.4	111.6
10a	140.8	142.6	141.0	141.7	141.5	140.1	144.5	142.8
N-CH_3		33.6		34.4	34.6		41.9	35.4
1-OCH_3					55.3	60.5	60.8	60.8
3-OCH_3					55.6			
4-OCH_3						61.4	61.4	
OCH_2O			101.9	102.2		102.9	102.2	102.0

① 化合物 1,4 在$(CD_3)_2SO$中测定；化合物 3,6,8 在 $CDCl_3 + CD_3OD(1+1)$中测定；化合物 5 在 $CDCl_3 + (CD_3)_2SO$ 中测定。

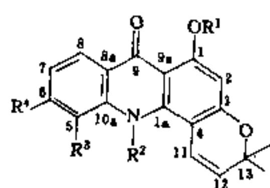


1. $R^1 = R^2 = R^3 = R^4 = R^5 = H$
2. $R^1 = R^2 = R^3 = R^4 = H, R^5 = CH_3$
3. $R^1 = R^4 = R^5 = H, R^2 + R^3 = OCH_2O$
4. $R^1 = R^4 = H, R^2 + R^3 = OCH_2O, R^5 = CH_3$
5. $R^1 = R^3 = OCH_3, R^2 = R^4 = H, R^5 = CH_3$
6. $R^1 = R^4 = OCH_3, R^2 + R^3 = OCH_2O, R^5 = H$
7. $R^1 = R^4 = OCH_3, R^2 + R^3 = OCH_2O, R^5 = CH_3$
8. $R^1 = OCH_3, R^2 + R^3 = OCH_2O, R^4 = H, R^5 = CH_3$

表 20-10 吖啶酮类生物碱 9～16 的13C-NMR 化学位移数据[28]①

C＼化合物	9	10	11	12	13	14	15	16
1	159.5	161.4	157.5	159.2	159.2	161.1	160.6	161.1
2	96.5	97.4	93.4	94.2	96.6	97.5	97.8	98.2
3	164.2	164.9	162.5	162.9	164.0	164.3	164.3	164.5
4	104.4	106.6	107.0	110.5	104.1	106.9	106.4	106.7
5	117.4	116.2	116.9	115.9	145.1	147.7	142.5	142.3
6	133.3	133.9	132.2	132.5	116.6	120.1	156.2	157.5
7	121.4	121.9	121.0	121.7	121.5	123.3	113.4	108.2
8	125.0	125.7	126.1	127.0	115.1	116.0	122.2	122.4
9	180.9	180.7	176.6	177.1	180.9	181.8	181.1	181.4
4a	141.0	144.6	140.2	146.7	136.6	148.5	147.4	147.7
8a	119.3	121.4	122.6	125.3	120.1	124.7	117.4	118.7
9a	98.1	100.9	99.9	103.0	97.8	102.1	102.3	102.5
10a	138.0	144.1	139.9	144.4	130.7	137.0	136.7	138.4
11	116.5	121.4	116.7	121.7	115.1	121.0	120.6	120.8
12	125.0	122.7	125.6	122.9	125.9	123.6	124.1	124.1
13	76.8	76.3	76.6	76.3	76.9	76.6	76.5	76.6
13-CH_3	27.7	26.8	27.6	26.8	27.6	27.1	27.0	27.1
N-CH_3		43.5		44.2		48.6	48.6	49.0
1-OCH_3			55.8	56.2				
5-OCH_3							59.8	60.3
6-OCH_3								56.3

① 化合物 9～11,13～15 在 $CDCl_3 + (CD_3)_2SO$ 中测定。

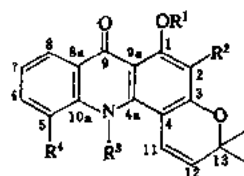


9. $R^1 = R^2 = R^3 = R^4 = H$
10. $R^1 = R^3 = R^4 = H, R^2 = CH_3$
11. $R^1 = CH_3, R^2 = R^3 = R^4 = H$
12. $R^1 = R^3 = CH_3, R^2 = R^4 = H$
13. $R^1 = R^2 = R^4 = H, R^3 = OH$
14. $R^1 = R^4 = H, R^2 = CH_3, R^3 = OH$
15. $R^1 = H, R^2 = CH_3, R^3 = OCH_3, R^4 = OH$
16. $R^1 = H, R^2 = CH_3, R^3 = R^4 = OCH_3$

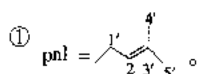
表 20-11　吖啶酮类生物碱 17～24 的 ^{13}C-NMR 化学位移数据[28]①

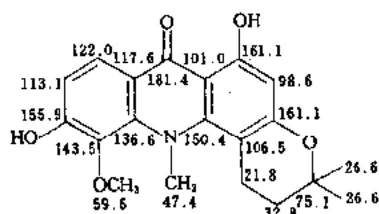
C \ 化合物	17	18	19	20	21	22	23	24
1	157.6	159.0	157.4	157.4	158.8	157.6	159.1	157.2
2	108.9	109.3	118.9	108.9	109.5	109.4	110.3	119.4
3	161.4	161.7	159.8	161.2	161.2	161.4	161.5	159.2
4	104.3	106.2	113.6	104.0	106.5	104.3	107.1	114.4
5	117.2	116.1	115.9	144.9	145.8	146.3	146.0	147.9
6	133.1	133.6	132.7	116.3	119.8	111.2	115.2	114.3
7	121.2	121.5	121.6	121.2	122.9	120.6	122.7	122.9
8	125.3	125.5	127.2	115.4	116.0	116.7	117.8	118.4
9	181.1	180.5	176.7	181.1	181.8	180.9	181.9	177.9
4a	140.9	144.4	144.8	134.7	148.4	134.3	150.5	150.8
8a	119.4	121.2	124.7	120.0	124.7	119.7	125.0	128.6
9a	97.9	100.5	106.5	97.4	101.9	97.4	102.2	108.1
10a	136.2	142.2	144.7	130.7	137.0	130.8	138.2	137.7
11	116.8	121.7	122.0	115.1	121.3	114.8	121.5	121.4
12	125.0	122.4	124.1	126.0	123.3	126.2	123.6	125.4
13	76.7	76.1	76.1	76.8	76.3	77.0	76.4	76.2
13-CH_3	27.7	26.7	26.9	27.6	27.0	27.7	27.1	27.1
N-CH_3		43.4	44.2		48.4		49.0	48.2
1-OCH_3			62.1					61.9
5-OCH_3						55.9	56.0	55.9
1′	21.2	21.4	22.5	21.1	21.3	21.4	21.5	22.5
2′	122.8	122.5	123.1	122.7	122.5	122.9	122.6	123.3
3′	130.5	130.6	130.9	130.3	130.6	130.5	131.0	130.8
4′	17.8	17.8	18.0	17.8	17.8	18.0	18.0	18.0
5′	25.7	25.7	25.8	25.7	25.7	25.9	25.9	25.8

① 化合物 17～18,20～21 在 $CDCl_3$ + $(CD_3)_2SO$ 中测定。

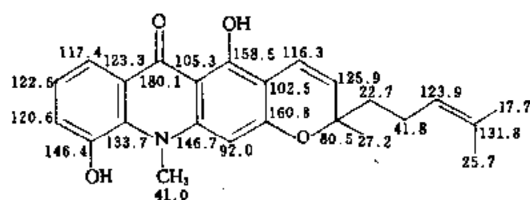


化合物	R¹	R²	R³	R⁴	化合物	R¹	R²	R³	R⁴
17	H	pnl①	H	H	21	H	pnl	CH_3	OH
18	H	pnl	CH_3	H	22	H	pnl	H	OCH_3
19	CH_3	pnl	H	H	23	H	pnl	CH_3	OCH_3
20	H	pnl	H	OH	24	CH_3	pnl	CH_3	OCH_3

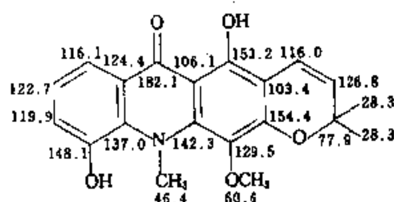
① pnl =  。



25[28]



26[28]

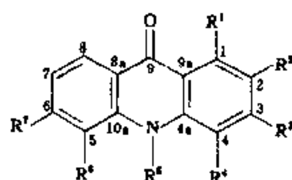


27[28]

表 20-12　吖啶酮类生物碱 28～35 的^{13}C-NMR 化学位移数据[28]①

C \ 化合物	28	29	30	31	32	33	34	35
1	162.7	163.7	163.0	159.5	162.7	164.6	165.2	159.4
2	97.1	93.3	93.4	109.0	98.6	94.2	94.1	93.5
3	164.3	165.3	165.0	161.4	162.9	165.4	165.9	160.0
4	106.4	106.9	108.9	107.2	107.2	90.2	90.7	129.8
5	116.4	116.3	148.6	148.6	142.6	138.8	138.7	148.2
6	133.6	133.8	119.9	119.6	154.6	156.4	157.7	119.9
7	121.0	121.2	122.7	122.4	112.0	112.7	107.4	122.5
8	125.4	125.9	116.1	116.0	122.5	122.4	122.9	115.7
9	180.8	181.7	182.9	182.5	182.0	179.7	180.3	181.9
4a	147.1	146.7	150.3	148.9	150.5	147.0	147.5	141.9
8a	121.0	121.2	124.8	124.7	118.2	116.1	117.6	124.1
9a	105.2	106.5	107.2	106.9	106.9	104.4	104.8	105.8
10a	145.6	146.1	138.4	138.1	136.0	135.3	137.0	137.2
N-CH$_3$	43.4	43.8	48.1	48.1	47.7	39.9	40.4	46.0
3-OCH$_3$		55.9	55.9			55.3	55.5	56.0
4-OCH$_3$								60.0
5-OCH$_3$					59.9	60.9	61.3	
6-OCH$_3$							56.3	
1′				21.6				
2′				122.6				
3′				132.5				
4′				17.9				
5′				25.7				
1″	26.9	27.1	26.3	26.7	26.6			
2″	124.6	124.5	123.8	123.3	123.3			
3″	131.1	131.6	131.3	133.4	135.2			
4″	18.0	18.1	18.0	18.1	18.1			
5″	25.5	25.6	25.7	25.7	25.8			

① 化合物 28,30,31,33,35 在 $CDCl_3$ + $(CD_3)_2SO$ 中测定。



化合物	R^1	R^2	R^3	R^4	R^5	R^6	R^7
28	OH	H	OH	pnl′	CH_3	H	H
29	OH	H	OCH_3	pnl′	CH_3	H	H
30	OH	H	OCH_3	pnl′	CH_3	OH	H
31	OH	pnl	OH	pnl′	CH_3	OH	H
32	OH	H	OH	pnl′	CH_3	OCH_3	OH
33	OH	H	OCH_3	H	CH_3	OCH_3	OH
34	OH	H	OCH_3	H	CH_3	OCH_3	OCH_3
35	OH	H	OCH_3	OCH_3	CH_3	OH	H

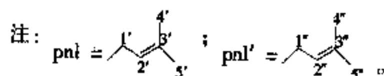
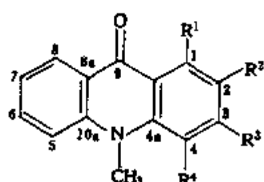
注：

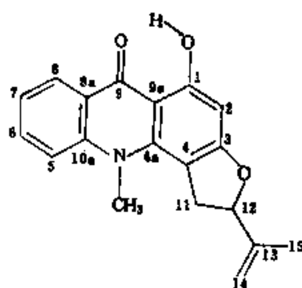
表 20-13 吖啶酮类生物碱 36～43 的^{13}C-NMR 化学位移数据[29,30]①

C \ 化合物	36	37	38	39	40	41	42	43
1	149.1	137.2	142.4	155.7	165.3	164.9	164.9	165.0
2	136.8	135.1	130.9	129.9	91.6	91.5	91.6	91.6
3	152.1	145.0	148.6	159.1	166.8	167.4	167.2	167.0
4	141.4	128.9	120.7	86.7	100.7	101.4	101.6	101.1
5	116.4	116.4	114.8	114.5	115.8	115.7	115.7	115.8
6	133.2	132.7	133.2	133.7	134.3	134.1	134.1	134.2
7	121.1	121.1	120.8	121.2	121.6	121.4	121.3	121.4
8	125.8	125.6	126.3	126.0	125.3	125.2	125.2	125.2
9	175.9	175.8	175.3	180.4	180.0	179.9	179.9	180.0
4a	138.8	136.5	133.1	140.1	143.1	143.1	143.1	143.1
8a	123.3	123.4	122.4	120.3	120.0	120.0	120.0	120.0
9a	115.1	113.9	112.7	105.8	105.3	105.0	105.1	105.1
10a	144.5	144.2	143.4	141.6	142.2	142.1	142.1	142.1
11					37.6	37.7	37.7	37.7
12					85.8	86.3	84.5	86.0
13					143.4	72.7	74.7	72.3
14					112.4	20.6	62.2	20.9
15					16.9	65.9	61.8	49.9
1-OCH_3	61.1	60.9	61.6					
2-OCH_3	61.3		60.7	60.6				
3-OCH_3	61.3			55.8				
4-OCH_3	61.5	60.5						
N-CH_3	41.5	41.6	37.2	33.8	35.9	31.4	31.2	31.5
—OCH_2O—		102.5	101.6					

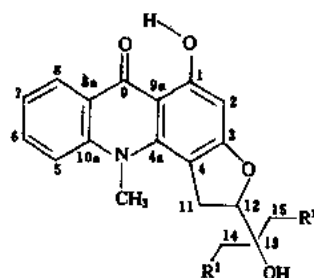
① 化合物 36～38 在$(CD_3)_2SO$中测定，化合物 39～43 在 $CDCl_3$ + CD_3OD 体积为 1 + 1 中测定。



36. $R^1 = R^2 = R^3 = R^4 = OCH_3$
37. $R^1 = R^4 = OCH_3, R^2 + R^3 = OCH_2O$
38. $R^1 = R^2 = OCH_3, R^3 + R^4 = OCH_2O$
39. $R^1 = OH, R^2 = R^3 = OCH_3, R^4 = H$



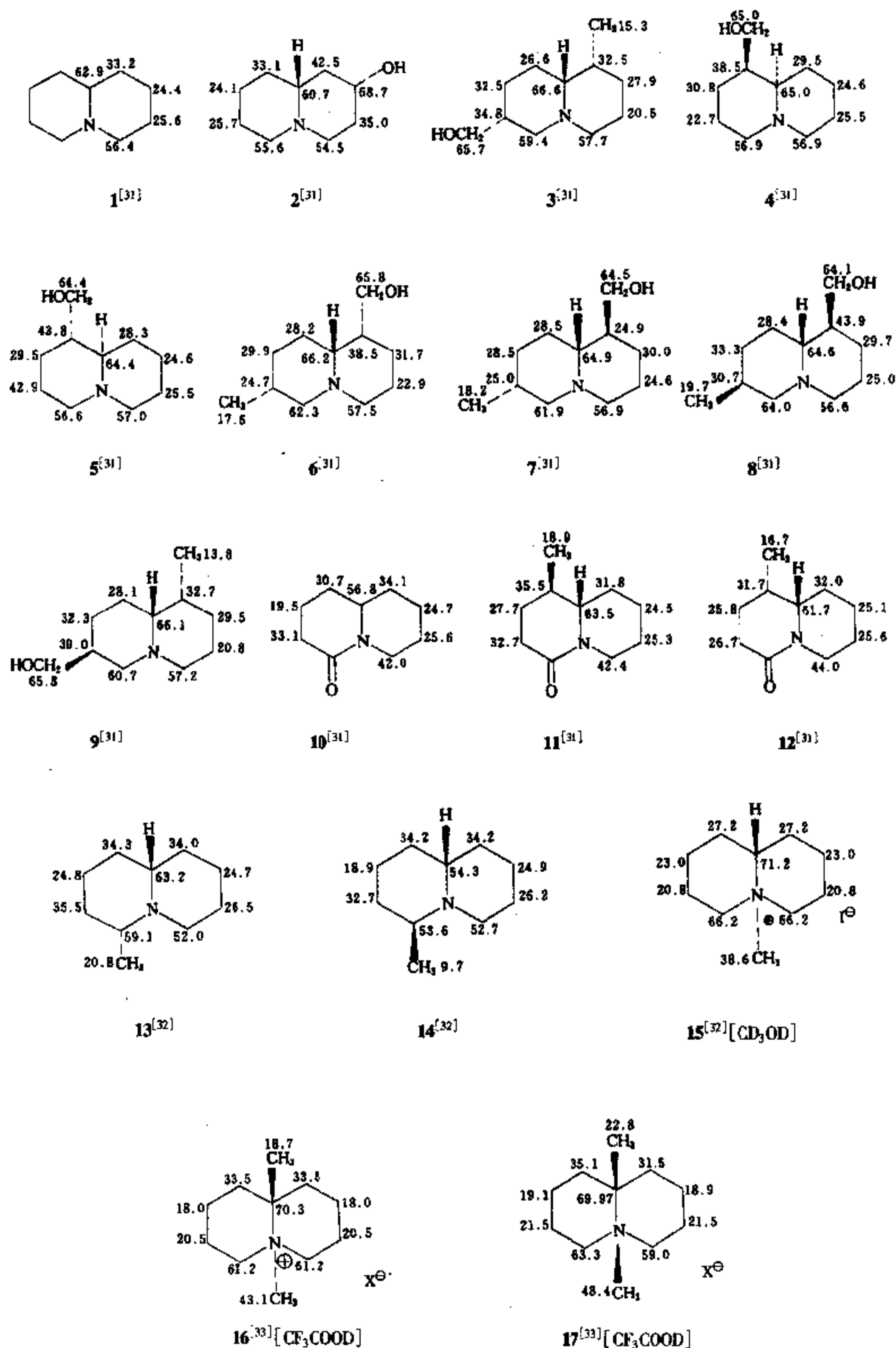
40



41. $R^1 = H, R^2 = OH$
42. $R^1 = R^2 = OH$
43. $R^1 = H, R^2 = Cl$

第五节　喹诺里西啶类生物碱的^{13}C-NMR 化学位移

一、简单喹诺里西啶类生物碱的^{13}C-NMR 化学位移



二、三环喹诺里西啶类生物碱的^{13}C-NMR 化学位移

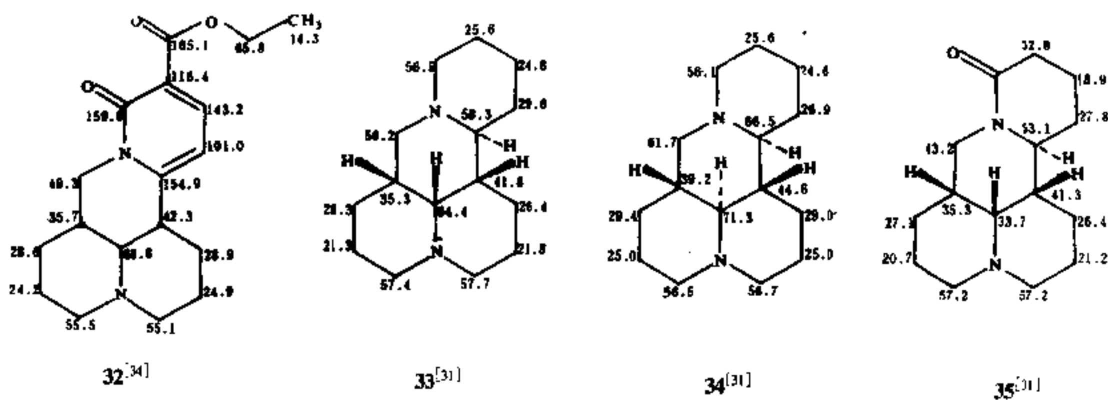
18[34] 19[34] 20[34] 21[34]

22[34] 23[34] 24[34] 25[34]

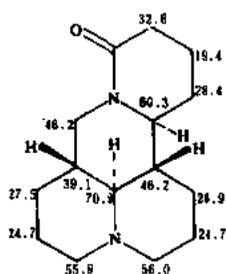
26[34] 27[34] 28[34]

29[34] 30[34] 31[34]

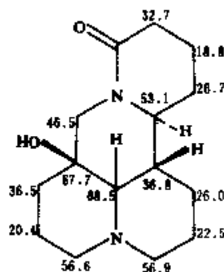
三、苦参碱类化合物的^{13}C-NMR 化学位移



32[34] 33[31] 34[31] 35[31]

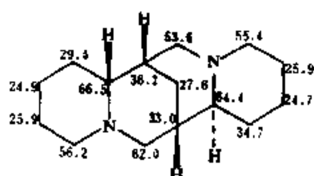


36[31]

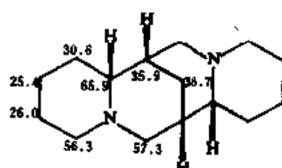


37[31]

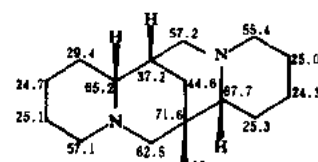
四、金雀儿碱型喹诺里西啶的^{13}C-NMR 化学位移



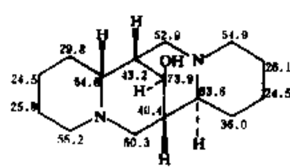
38[31]



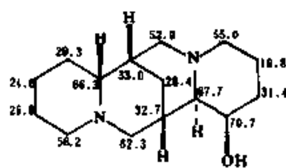
39[31]



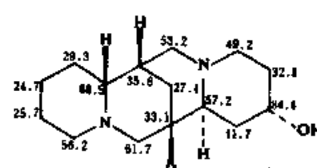
40[31]



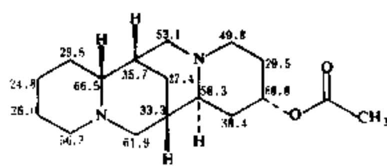
41[31]



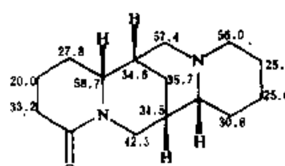
42[31]



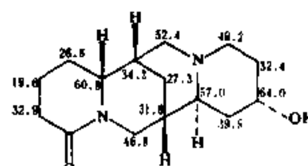
43[31]



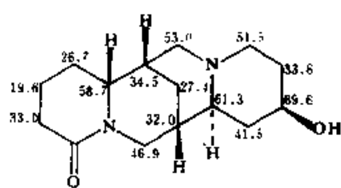
44[31]



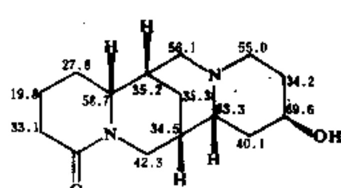
45[31]



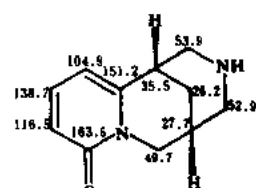
46[31]



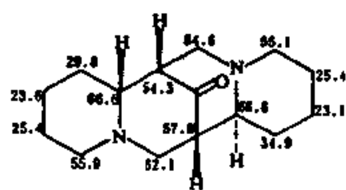
47[31]



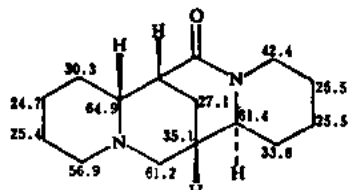
48[31]



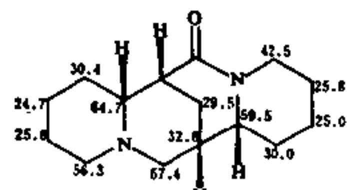
49[31]



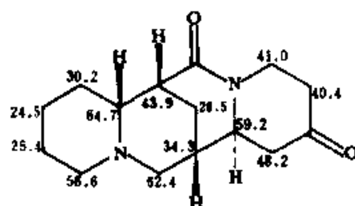
50[31]



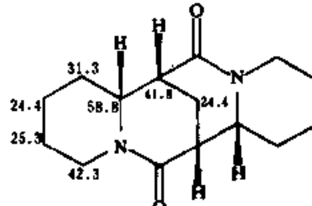
51[31]



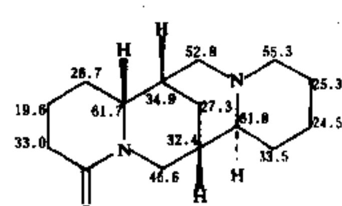
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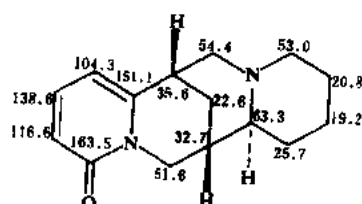
53[31]



54[31]

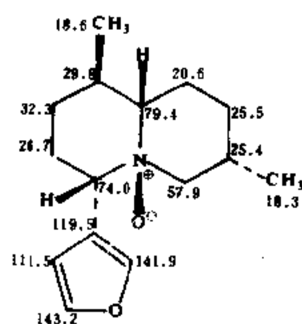


55[31]

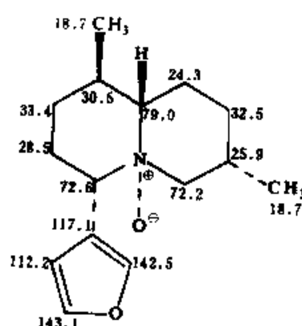


56[31]

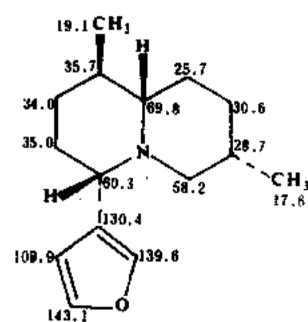
五、呋喃喹诺里西啶的^{13}C-NMR化学位移



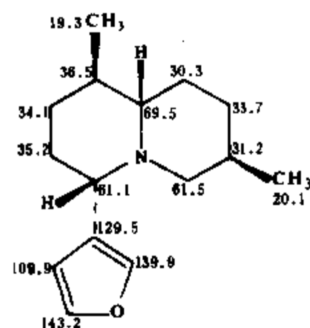
57[35]



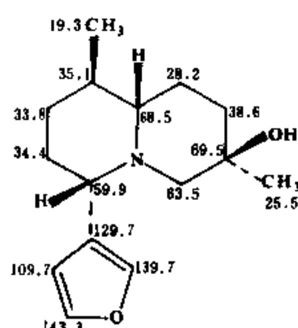
58[35]



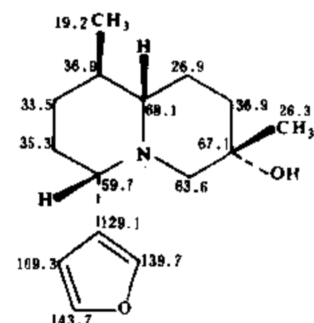
59[39]



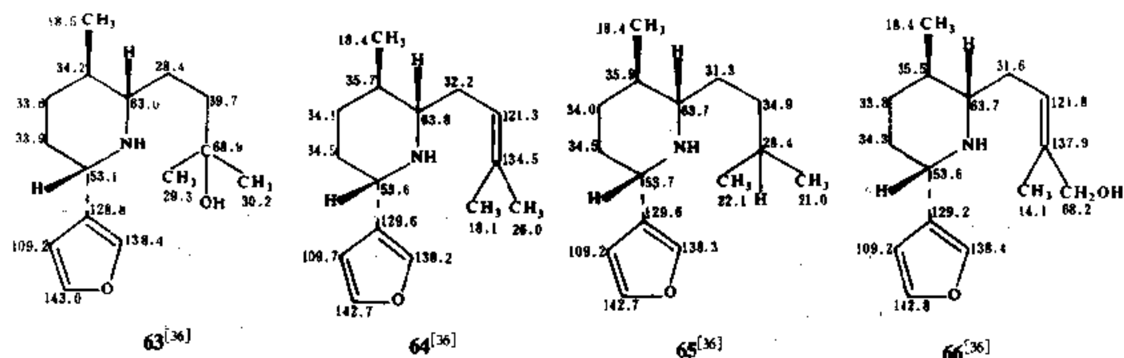
60[35]



61[35]



62[35]



63[36]　64[36]　65[36]　66[36]

六、石松碱类化合物的^{13}C-NMR化学位移

67[37]　68[37]　69[37]

71[37]　70[37]　72[37]

73[37]　74[37]

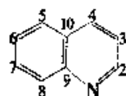
第六节　喹啉类生物碱的^{13}C-NMR化学位移

一、简单喹啉的^{13}C-NMR化学位移

表 20-14　简单喹啉 1～13 的^{13}C-NMR化学位移数据[16,38～40]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12①	13
2	150.2	158.2	152.2	149.8	149.3	149.0	148.1	148.2	149.9	147.8	143.1	150.6	144.2
3	120.9	121.7	130.1	121.6	120.8	120.6	120.0	120.6	119.6	121.2	140.2	119.8	141.6
4	135.7	135.6	134.2	143.9	135.0	135.8	131.9	135.3	135.8	134.5	114.6	131.0	132.4
5	127.6	127.3	127.1	123.6	131.4	125.8	131.8	124.6	124.7	105.1	125.8	145.5	133.6
6	126.4	125.4	126.3	126.1	135.9	126.1	126.4	135.7	129.3	157.7	126.8	109.2	129.0
7	129.2	129.1	128.2	128.8	126.5	129.4	128.9	131.8	134.1	122.1	125.3	130.8	130.0
8	129.4	128.7	129.2	129.8	129.1	137.1	134.8	136.5	136.9	130.8	128.8	118.6	130.1
9	148.3	147.9	146.6	147.8	147.0	147.5	147.5	146.0	147.3	144.5	142.4	150.3	150.3
10	128.2	126.4	128.1	128.0	128.0	128.2	127.3	128.3	126.5	129.3	126.2	119.1	126.2
CH_3		25.1	18.4	18.2	21.2	18.1	18.1	21.4	20.5				
OCH_3							18.1	18.0	13.3	55.1			

① 化合物 12 在$(CD_3)_2CO$中测定。



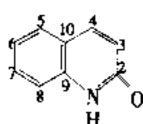
1. —
2. 2-CH_3
3. 3-CH_3
4. 4-CH_3
5. 6-CH_3
6. 8-CH_3
7. 5-CH_3,8-CH_3
8. 6-CH_3,8-CH_3
9. 7-CH_3,8-CH_3
10. 6-OCH_3
11. 3-NH_2
12. 5-NH_2
13. 3-NO_2

二、喹啉-2-酮的^{13}C-NMR化学位移

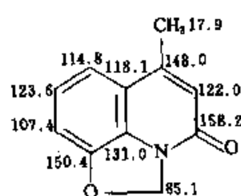
表 20-15　喹啉-2-酮 14～27 的^{13}C-NMR化学位移数据[41～43]①

C \ 化合物	14	15	16	17	18	19	20	21	22	23	24	25	26	27
2	162.0	161.6	161.9	162.4	162.0	161.5	161.9	161.8	164.5	161.0	161.6	161.7	161.6	163.1
3	121.7	120.9	121.7	121.5	121.1	120.8	119.8	120.6	120.4	121.6	119.7	120.6	121.1	121.3
4	140.1	147.7	139.9	140.7	146.3	147.4	147.7	148.1	149.0	149.4	147.3	147.9	145.2	145.8
5	127.8	124.5	127.3	125.9	125.1	124.1	124.4	122.5	122.8	135.9	124.5	122.1	115.9	117.5
6	121.9	121.5	130.6	121.5	121.9	130.4	123.0	121.2	138.4	127.2	129.8	130.1	121.2	122.3
7	130.2	130.1	131.4	131.5	130.4	131.3	140.2	131.4	130.7	140.5	139.3	132.7	109.5	113.7
8	115.2	115.4	115.0	123.4	114.4	115.4	115.2	123.5	116.8	114.4	115.8	123.4	148.0	148.7
9	139.0	138.7	136.8	137.3	139.8	136.6	138.8	137.0	136.4	139.0	136.9	135.0	128.0	131.3
10	119.1	119.6	119.1	119.2	121.3	119.5	117.6	119.7	120.4	116.9	117.7	117.6	120.3	123.4
CH_3		18.4	20.3	17.2	18.8	18.5	18.4	18.7	19.1	20.7	18.4	18.8	19.1	19.5
					29.1	20.6	21.2	17.0		24.2	19.0	20.4		35.3
										24.9	19.6	17.2		
CH_2CH_3									<8.7,15.8					
OCH_3													55.8	56.8

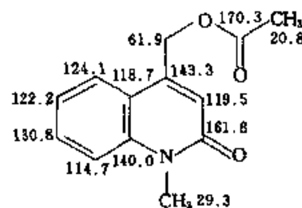
① 化合物 14～17,19～25 在$(CD_3)_2SO + CDCl_3$体积比为(9＋1)中测定。



14. —
15. 4-CH_3
16. 6-CH_3
17. 8-CH_3
18. 1-CH_3,4-CH_3
19. 4-CH_3,6-CH_3
20. 4-CH_3,7-CH_3
21. 4-CH_3,8-CH_3
22. 4-CH_3,6-CH_2CH_3
23. 4-CH_3,5-CH_3,7-CH_3
24. 4-CH_3,6-CH_3,7-CH_3
25. 4-CH_3,6-CH_3,8-CH_3
26. 4-CH_3,8-OCH_3
27. 1-CH_3,4-CH_3,8-OCH_3



28[43]



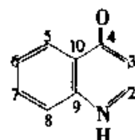
29[43]

三、喹啉-4-酮的^{13}C-NMR 化学位移

表 20-16　喹啉-4-酮 30～37 的^{13}C-NMR 化学位移数据[42]①

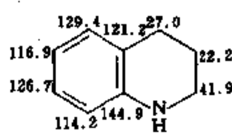
C \ 化合物	30	31	32	33	34	35	36	37
2	139.5	149.5	147.7	149.1	149.9	148.1	149.4	149.7
3	108.8	108.4	110.2	108.1	108.7	110.7	108.5	108.3
4	177.2	176.8	179.6	176.7	177.0	180.0	177.0	177.1
5	125.0	124.8	139.1	124.1	122.3	136.8	122.1	122.0
6	123.1	122.6	125.0	131.8	122.8	124.8	133.6	124.9
7	131.5	131.3	130.3	132.6	132.3	131.4	131.3	139.3
8	118.4	117.7	115.8	117.6	125.8	123.2	125.6	123.2
9	140.1	140.2	141.8	138.2	138.8	140.3	136.9	138.9
10	125.9	124.6	122.8	124.5	124.8	123.2	124.8	123.2
CH_3		19.5	18.9	19.4	19.8	19.4	19.7	19.8
			23.1	20.7	17.5	23.3	20.5	20.4
						17.7	17.4	13.1

① 化合物 30～37 在$(CD_3)_2SO + CDCl_3$ 体积比为(9＋1)中测定。

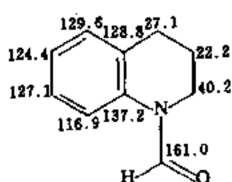


30. —
31. 2-CH_3
32. 2-CH_3,5-CH_3
33. 2-CH_3,6-CH_3
34. 2-CH_3,8-CH_3
35. 2-CH_3,5-CH_3,8-CH_3
36. 2-CH_3,6-CH_3,8-CH_3
37. 2-CH_3,7-CH_3,8-CH_3

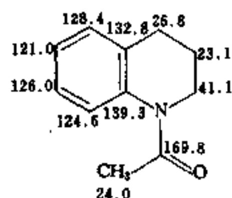
四、氢化喹啉类化合物的^{13}C-NMR 化学位移



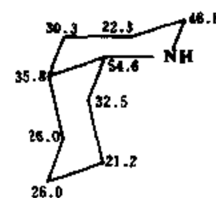
38[44]



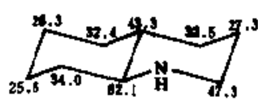
39[44]



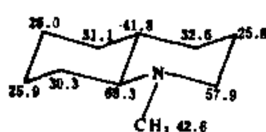
40[44]



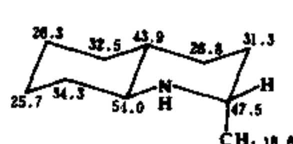
41[45]



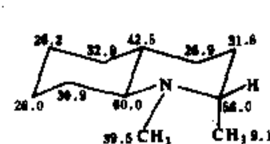
42[45]



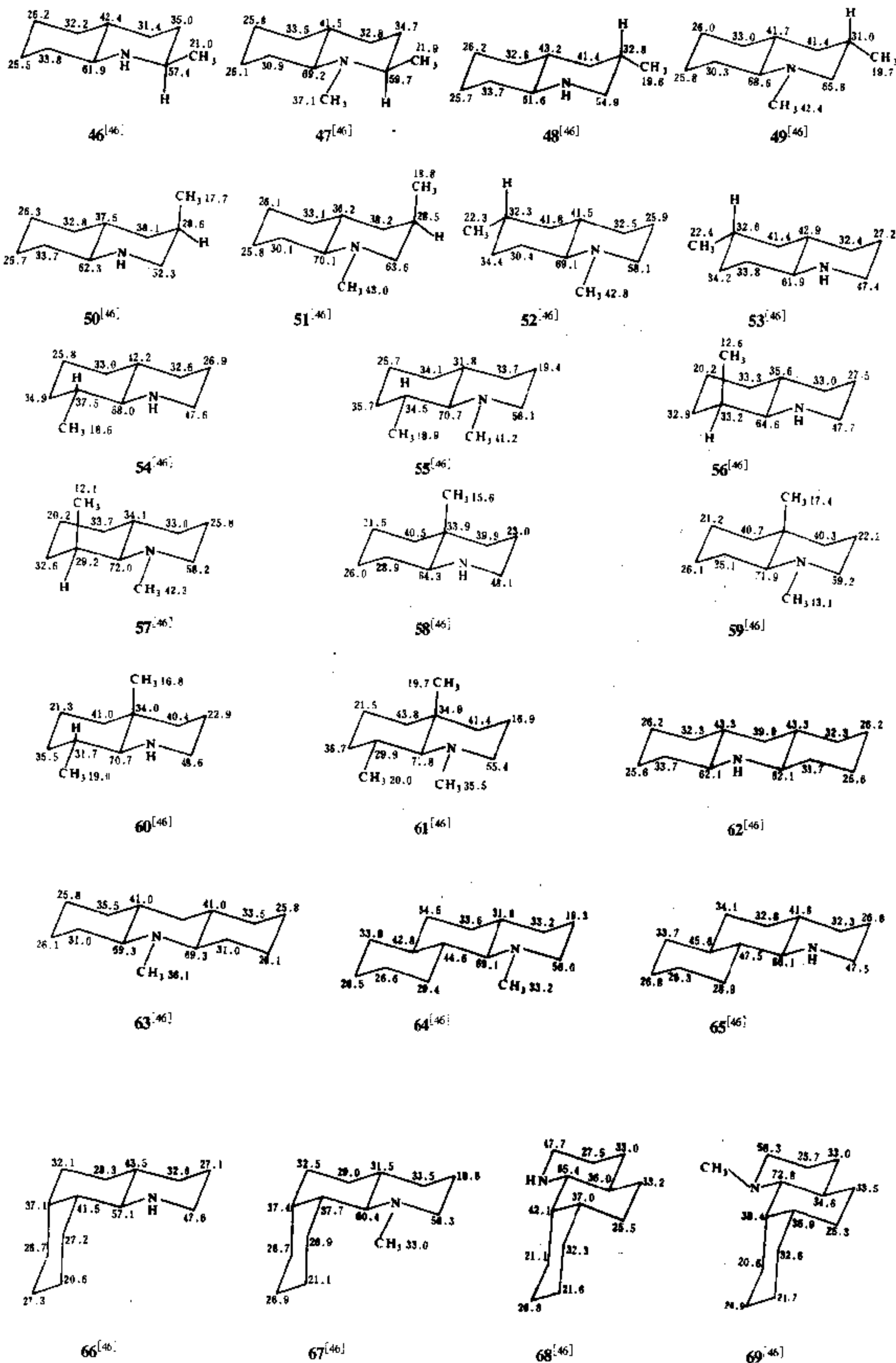
43[46]



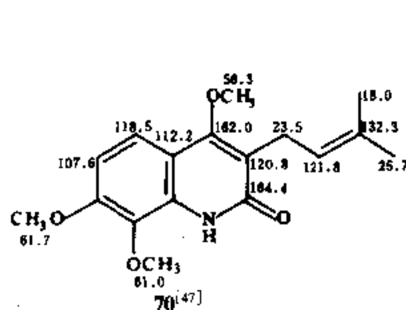
44[46]



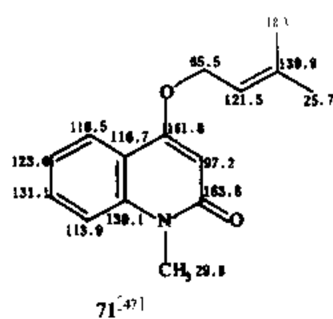
45[46]



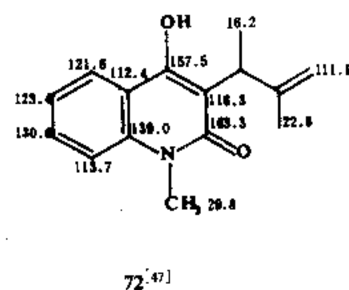
五、多取代喹啉类化合物的^{13}C-NMR化学位移



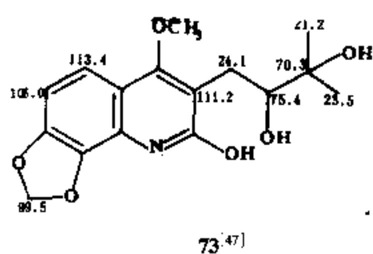
70[47]



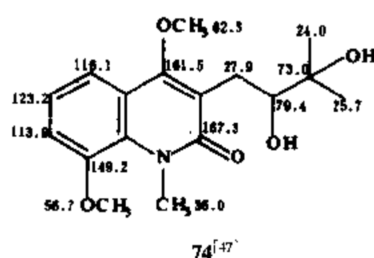
71[47]



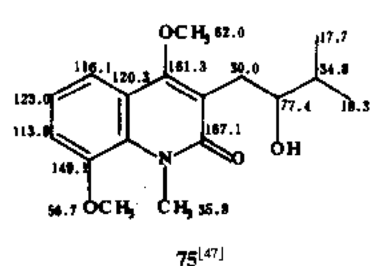
72[47]



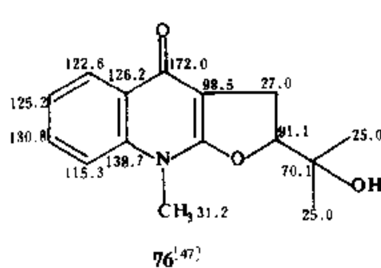
73[47]



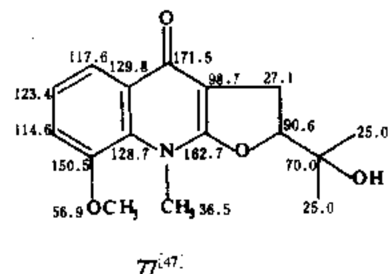
74[47]



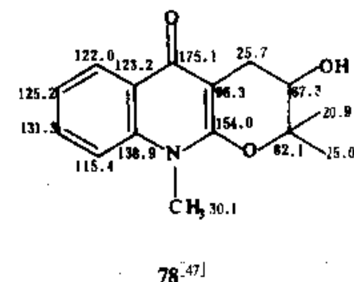
75[47]



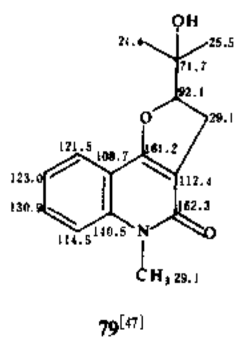
76[47]



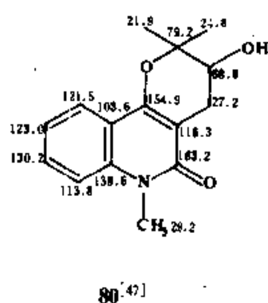
77[47]



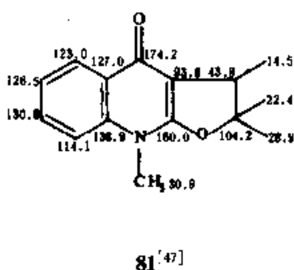
78[47]



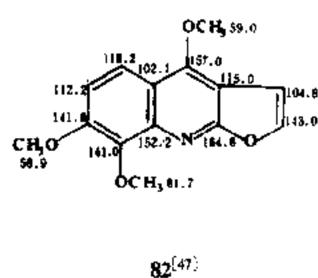
79[47]



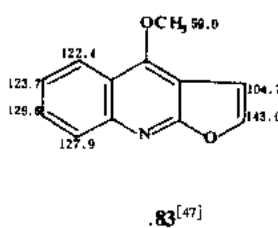
80[47]



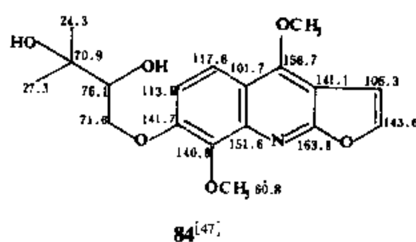
81[47]



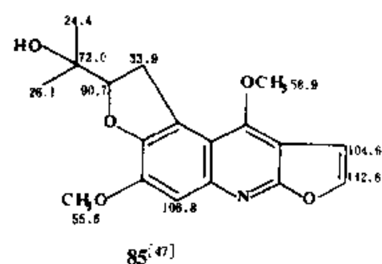
82[47]



83[47]

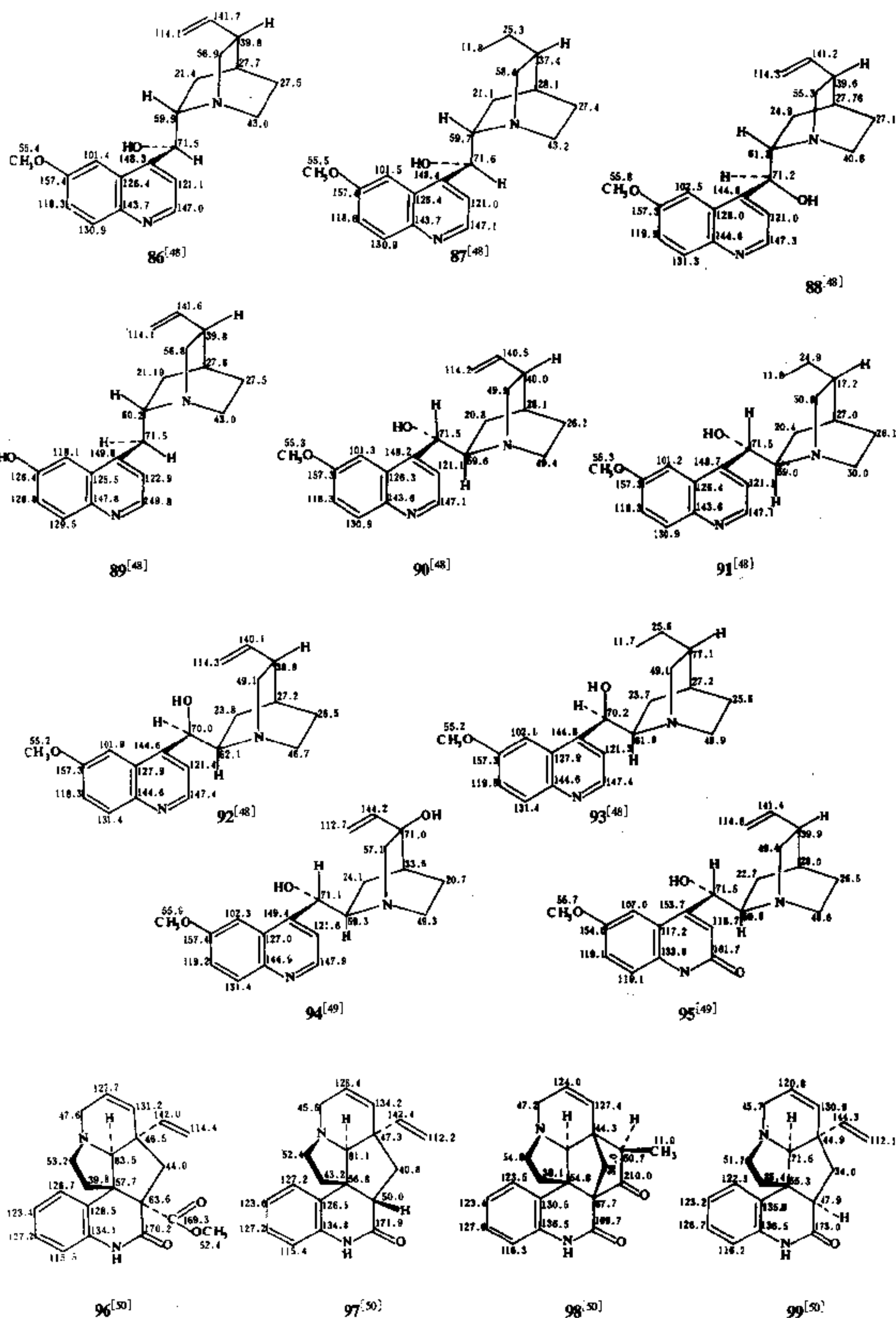


84[47]



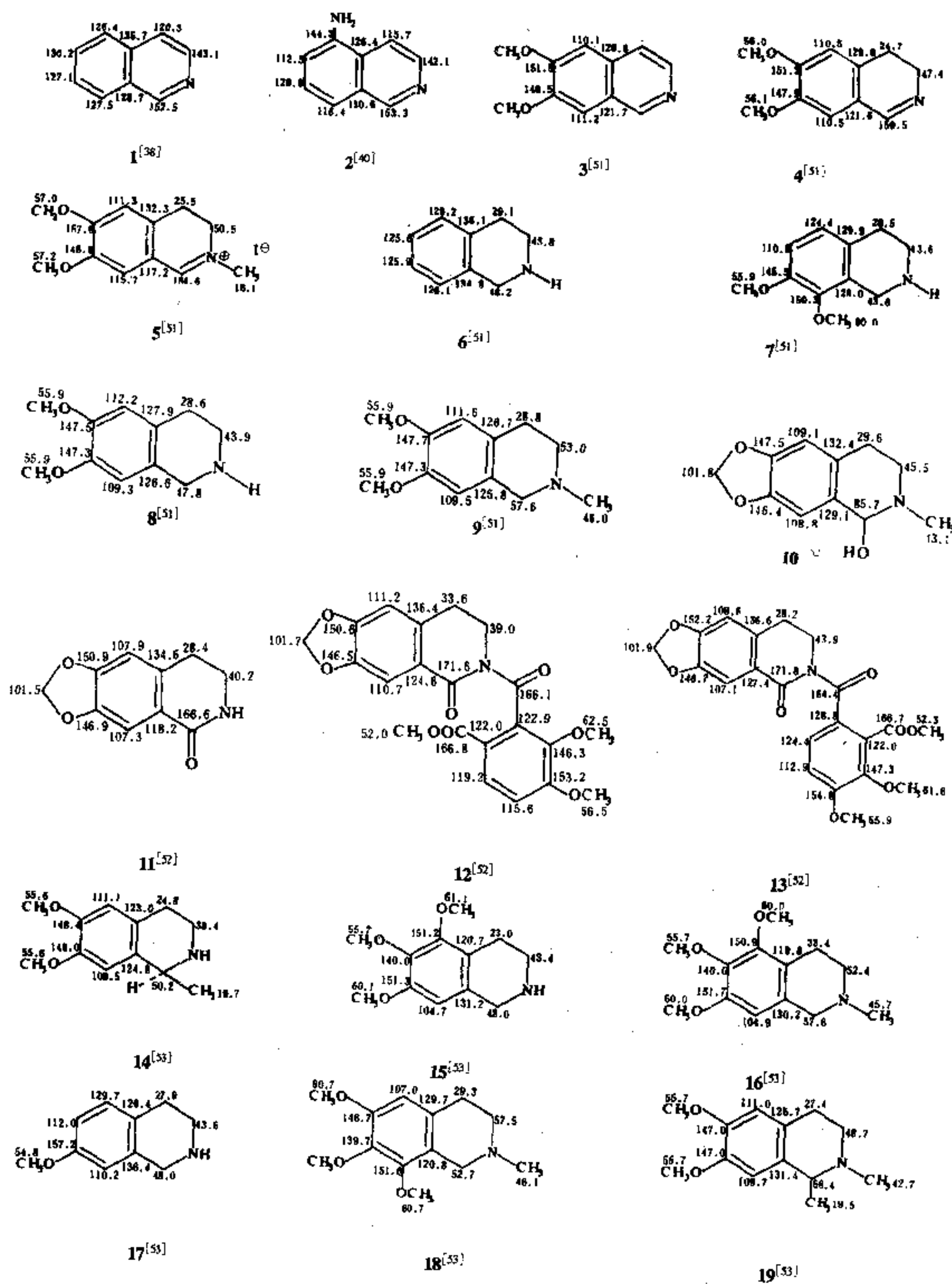
85[47]

六、金鸡纳生物碱的13C-NMR化学位移



第七节 异喹啉类生物碱的^{13}C-NMR 化学位移

一、简单异喹啉的^{13}C-NMR 化学位移



二、苄基异喹啉类生物碱的^{13}C-NMR化学位移

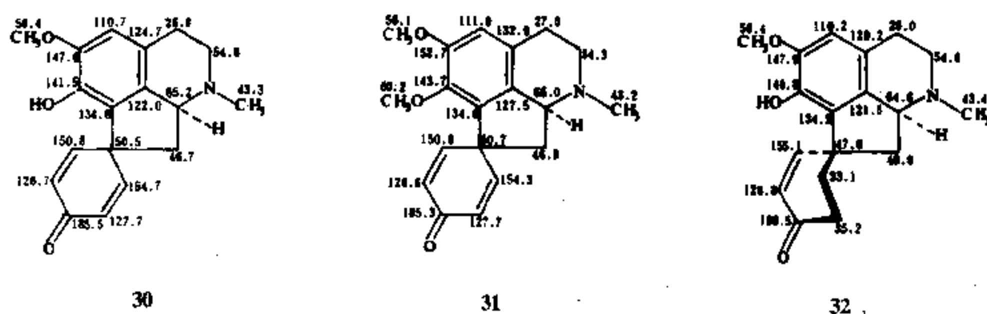
20　　21　　22

23　　24　　25

26　　27

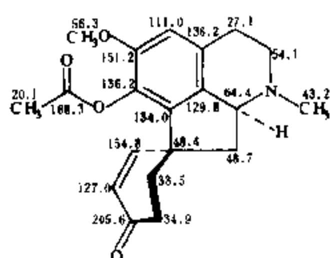
28　　29

三、原阿朴菲类生物碱的^{13}C-NMR化学位移[54]❶

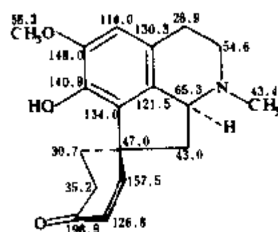


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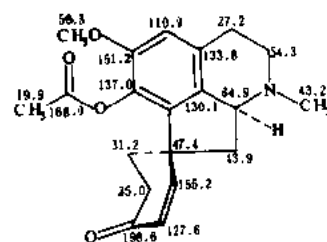
❶ 化合物30~46在$(CD_3)_2SO$中测定。



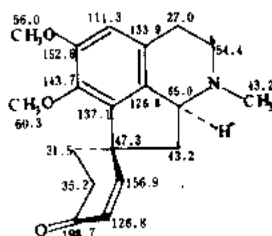
33



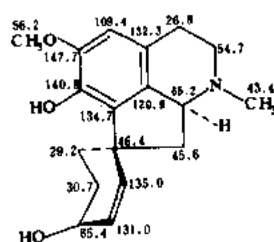
34



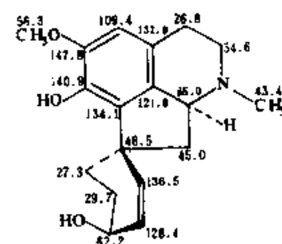
35



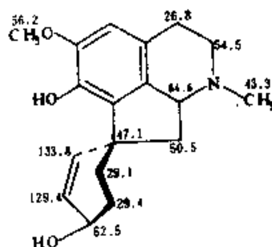
36



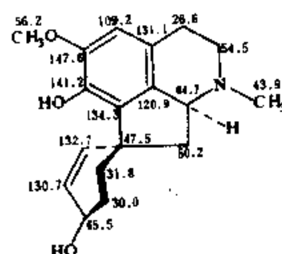
37



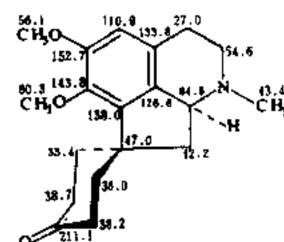
38



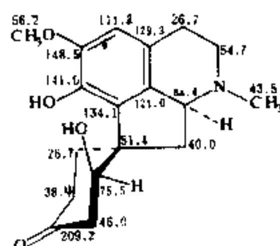
39



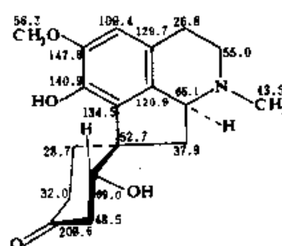
40



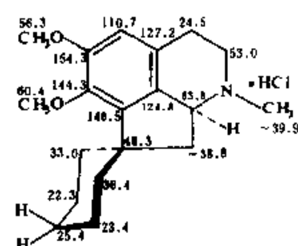
41



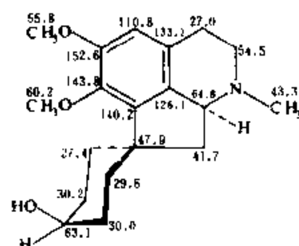
42



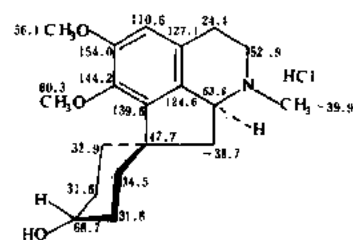
43



44

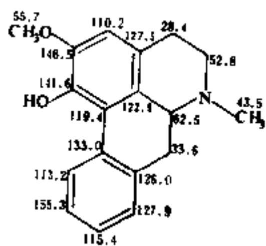


45

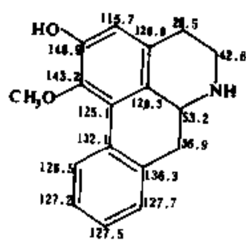


46

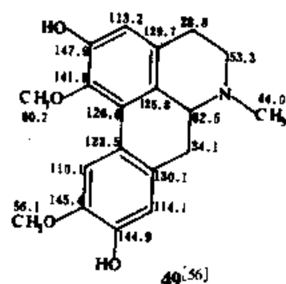
四、阿朴菲类生物碱的^{13}C-NMR 化学位移



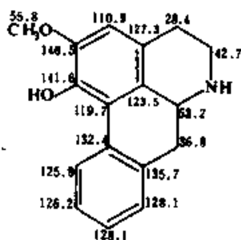
47[55][$(CD_3)_2SO$]



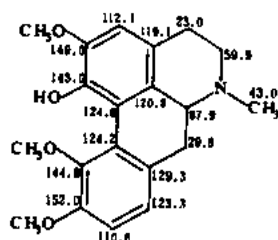
48[55][$(CD_3)_2SO$]



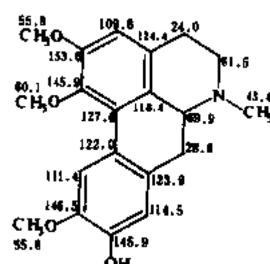
49[56]



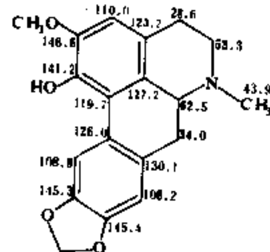
50[55][$(CD_3)_2SO$]



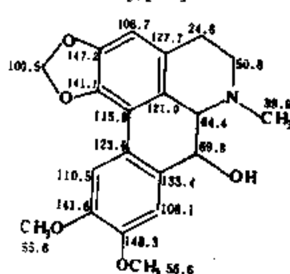
51[57][$(CD_3)_2SO$]



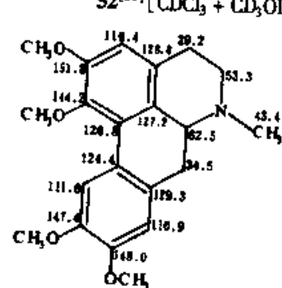
52[56][$CDCl_3 + CD_3OD$]



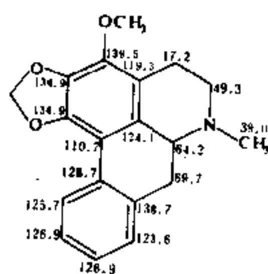
53[57][$(CD_3)_2SO$]



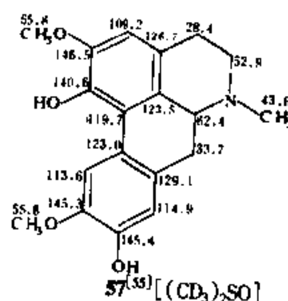
54[55][$(CD_3)_2SO$]



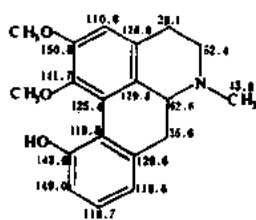
55[57]



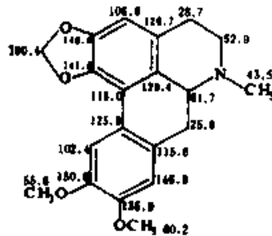
56[57]



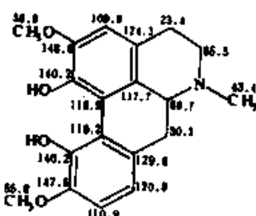
57[55][$(CD_3)_2SO$]



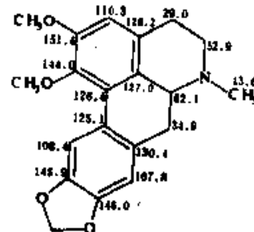
58[57]



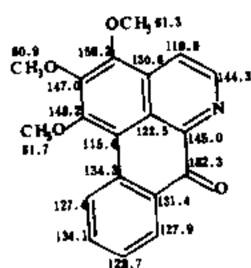
59[55][$(CD_3)_2SO$]



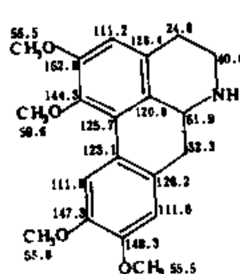
60[56][$CDCl_3 + CF_3COOH$]



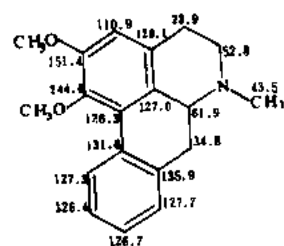
61[57]



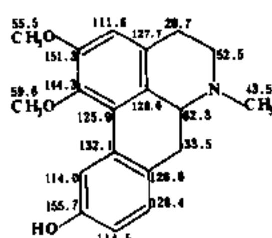
62[58][$CDCl_3 + CD_3OD$]



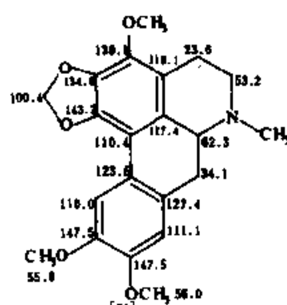
63[55][$(CD_3)_2SO$]



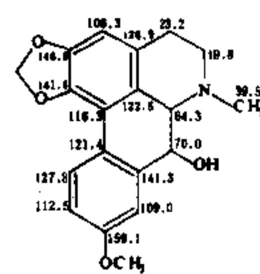
64[57]



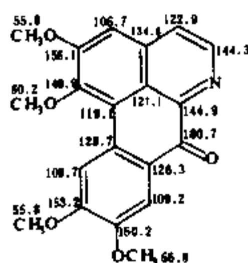
65[55][$(CD_3)_2SO$]



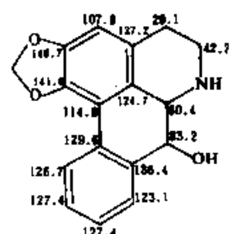
66[56]



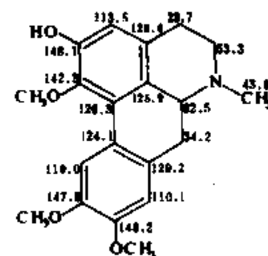
67[57]



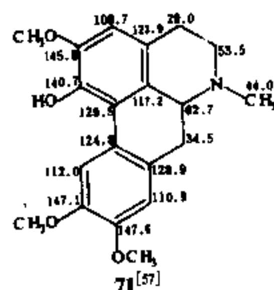
68[58][$CDCl_3 + CD_3OD$]



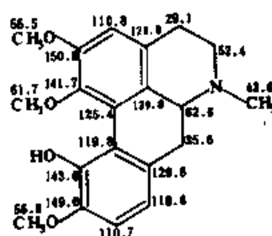
69[57]



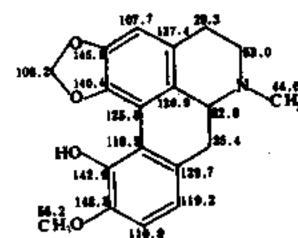
70[57]



71[57]

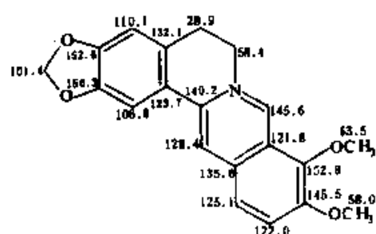


72

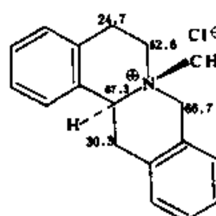


73

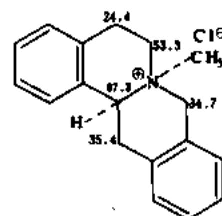
五、原小檗碱类生物碱的^{13}C-NMR 化学位移



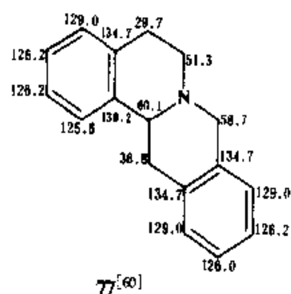
74



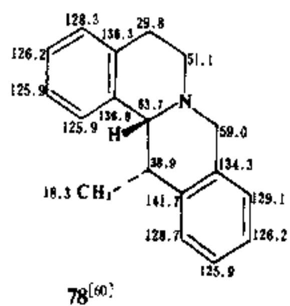
75[59][CD_3OD]



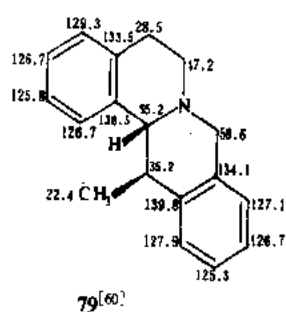
76[59][CD_3OD]



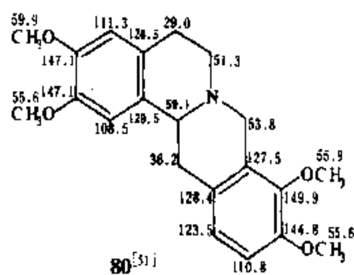
77[60]



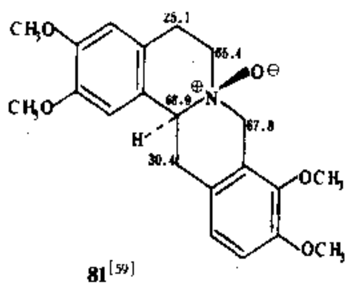
78[60]



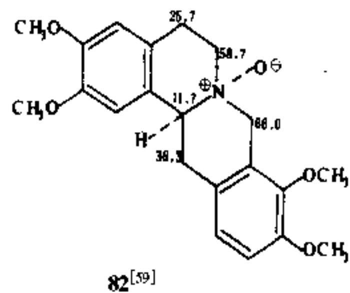
79[60]



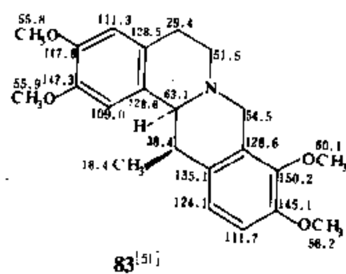
80[51]



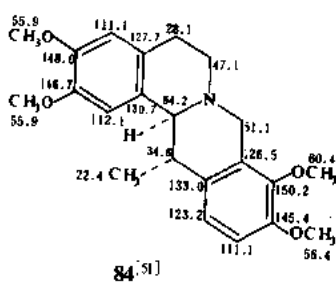
81[59]



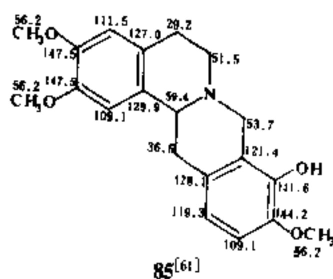
82[59]



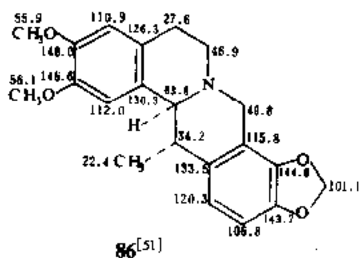
83[51]



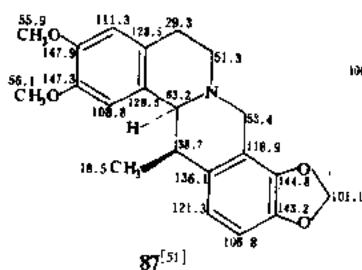
84[51]



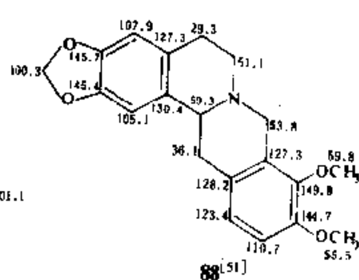
85[61]



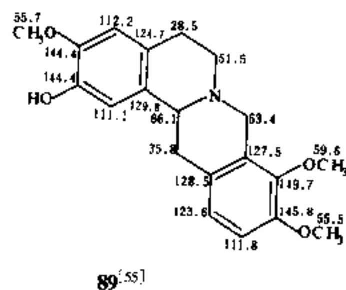
86[51]



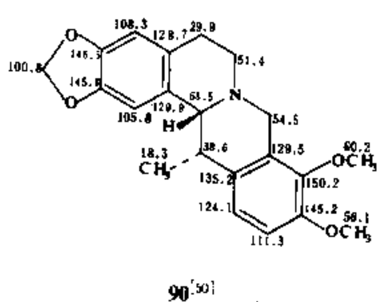
87[51]



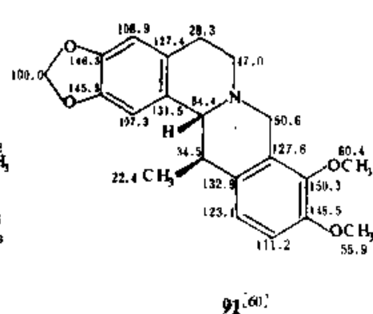
88[51]



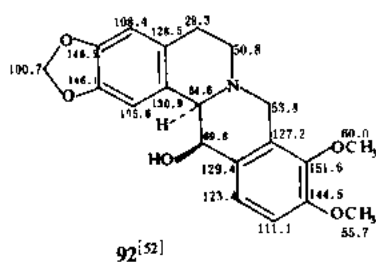
89[55]



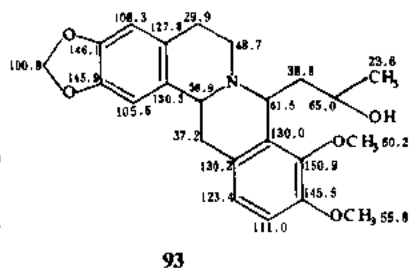
90[50]



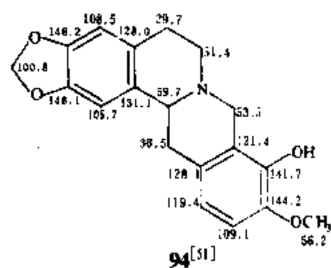
91[60]



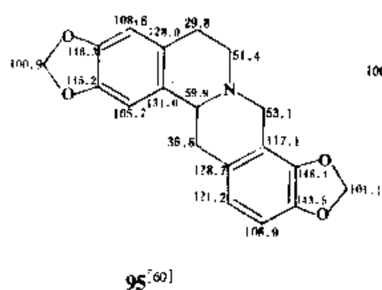
92[52]



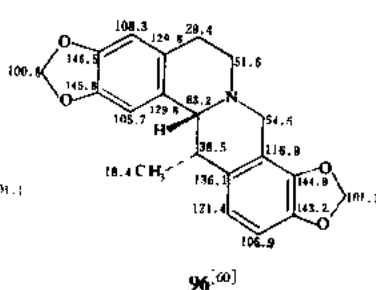
93



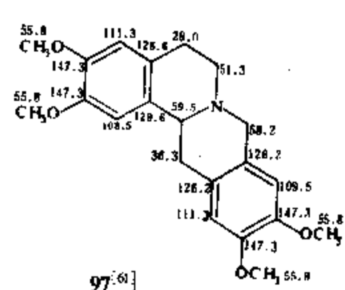
94[51]



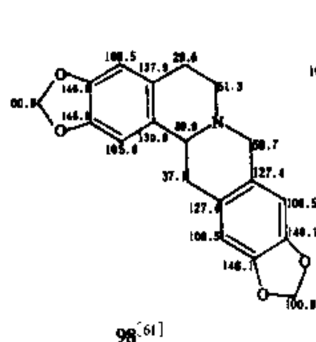
95[60]



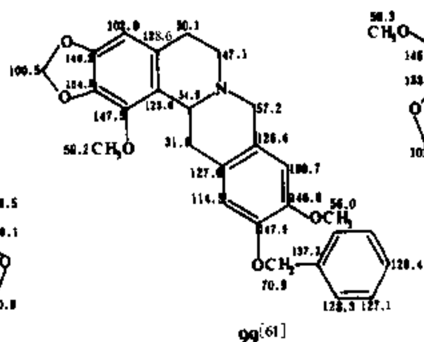
96[60]



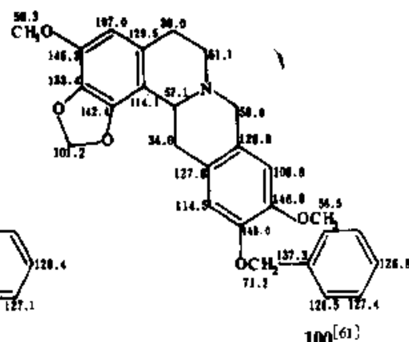
97[61]



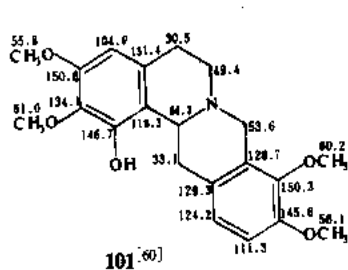
98[61]



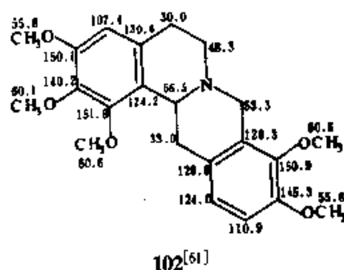
99[61]



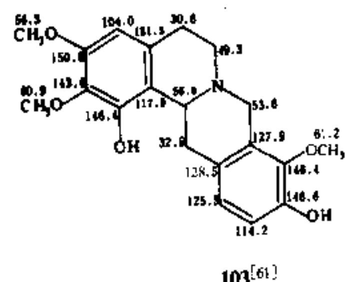
100[61]



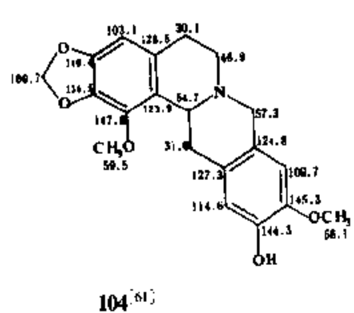
101[60]



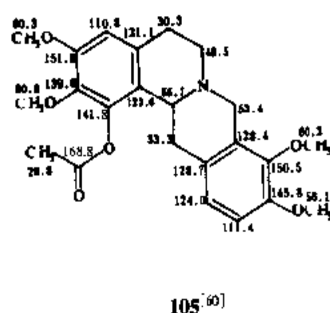
102[61]



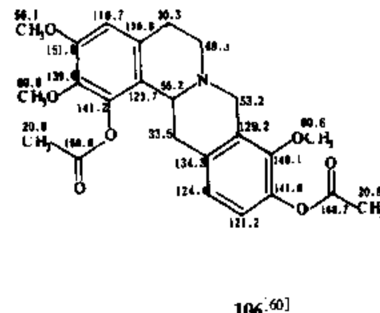
103[61]



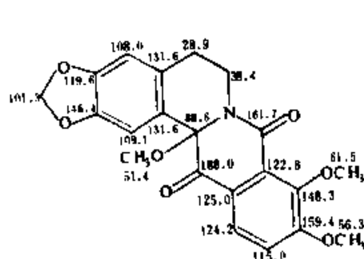
104[61]



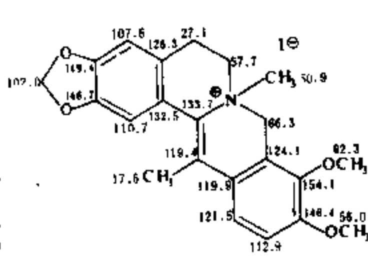
105[60]



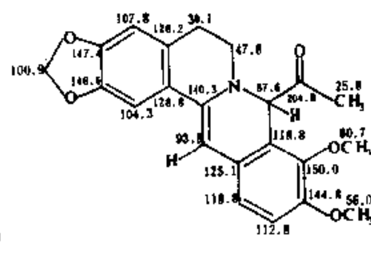
106[60]



107

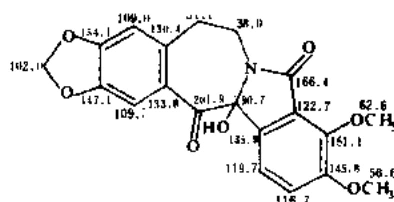


108

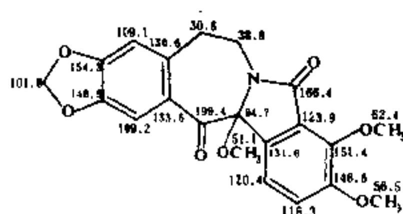


109

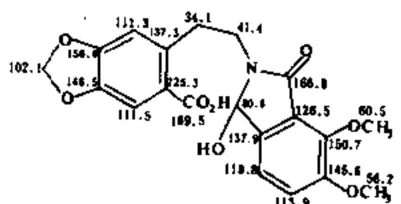
六、酰胺型异喹啉生物碱的^{13}C-NMR 化学位移



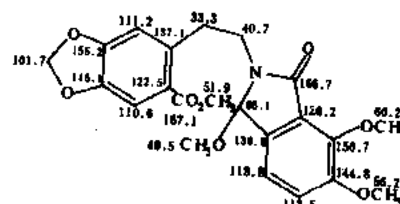
110



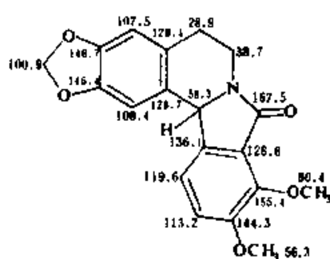
111



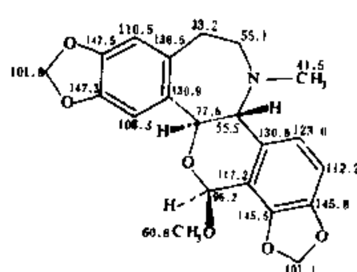
112



113

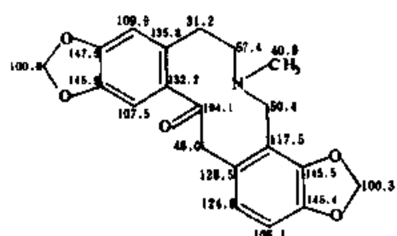


114

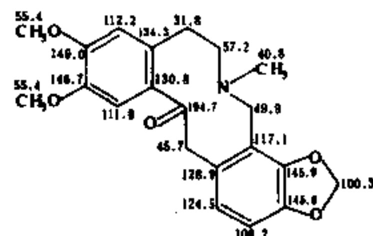


115

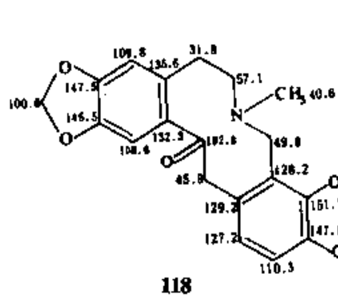
七、普托品类生物碱的^{13}C-NMR 化学位移



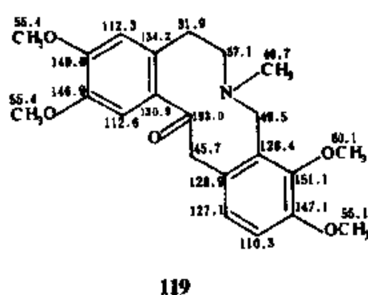
116



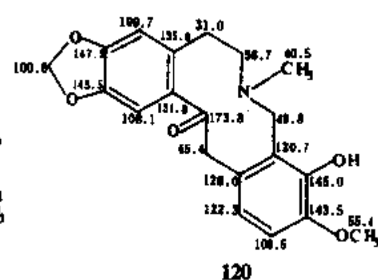
117



118

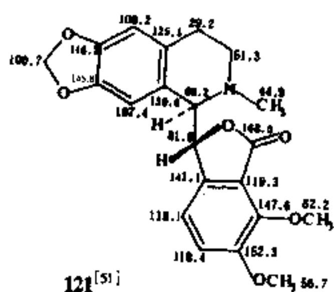


119

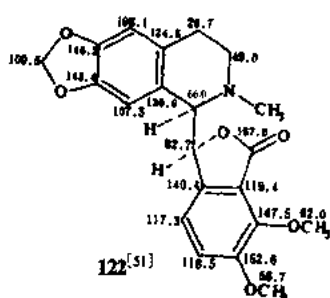


120

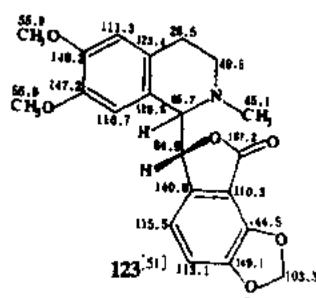
八、苯酞异喹啉类生物碱的¹³C-NMR 化学位移



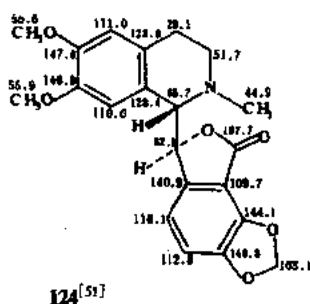
121[51]



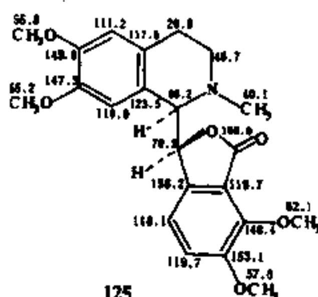
122[51]



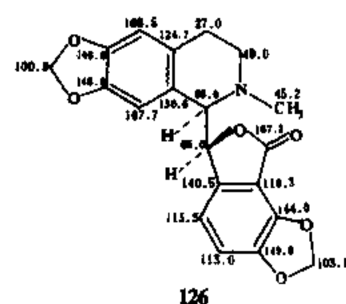
123[51]



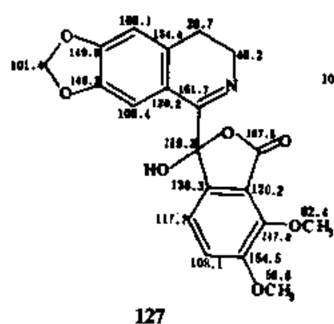
124[51]



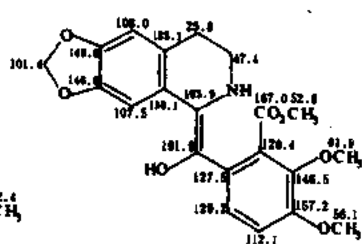
125



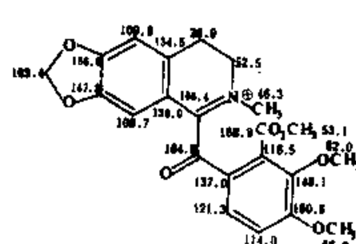
126



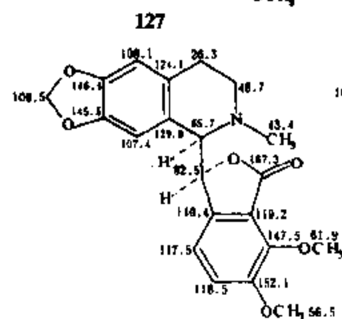
127



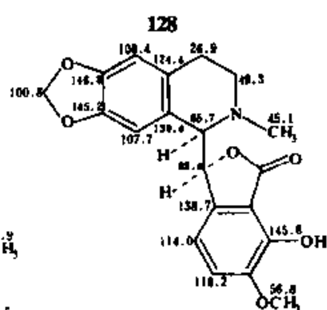
128



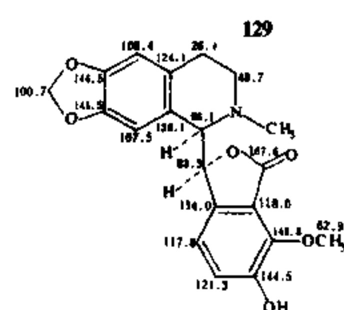
129



130[51]

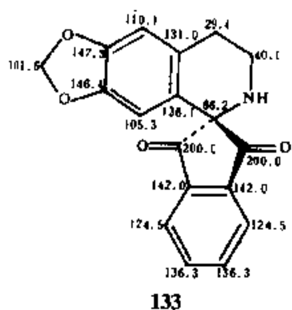


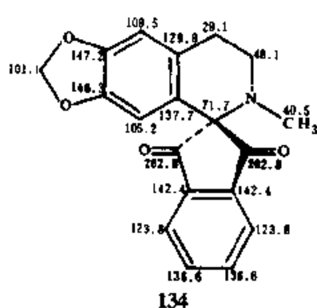
131[64]

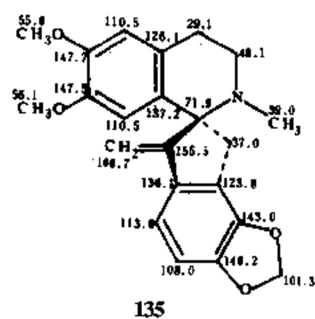


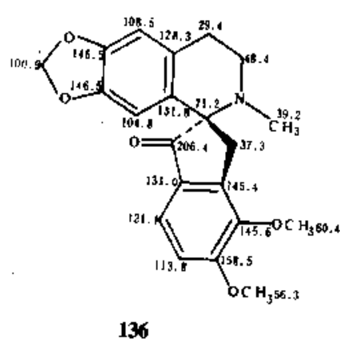
132[64]

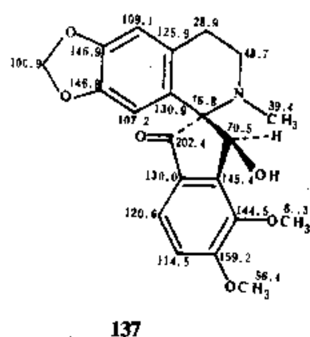
九、螺环苄基异喹啉类生物碱的^{13}C-NMR化学位移[62]

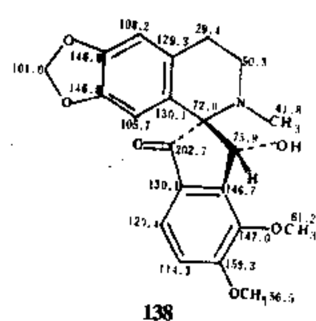

133

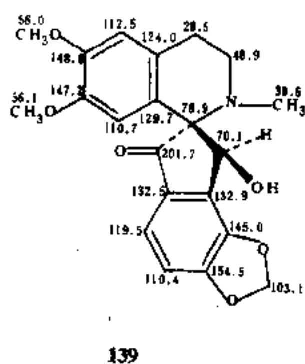

134

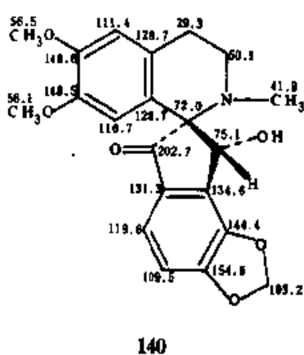

135

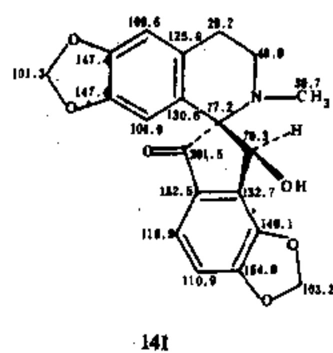

136

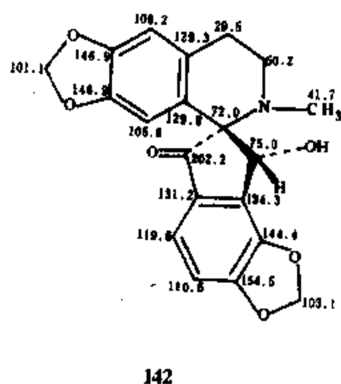

137

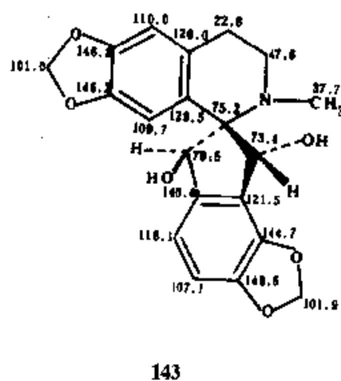

138

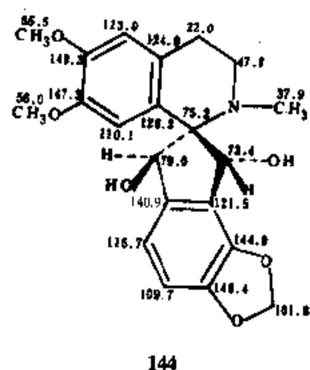

139


140

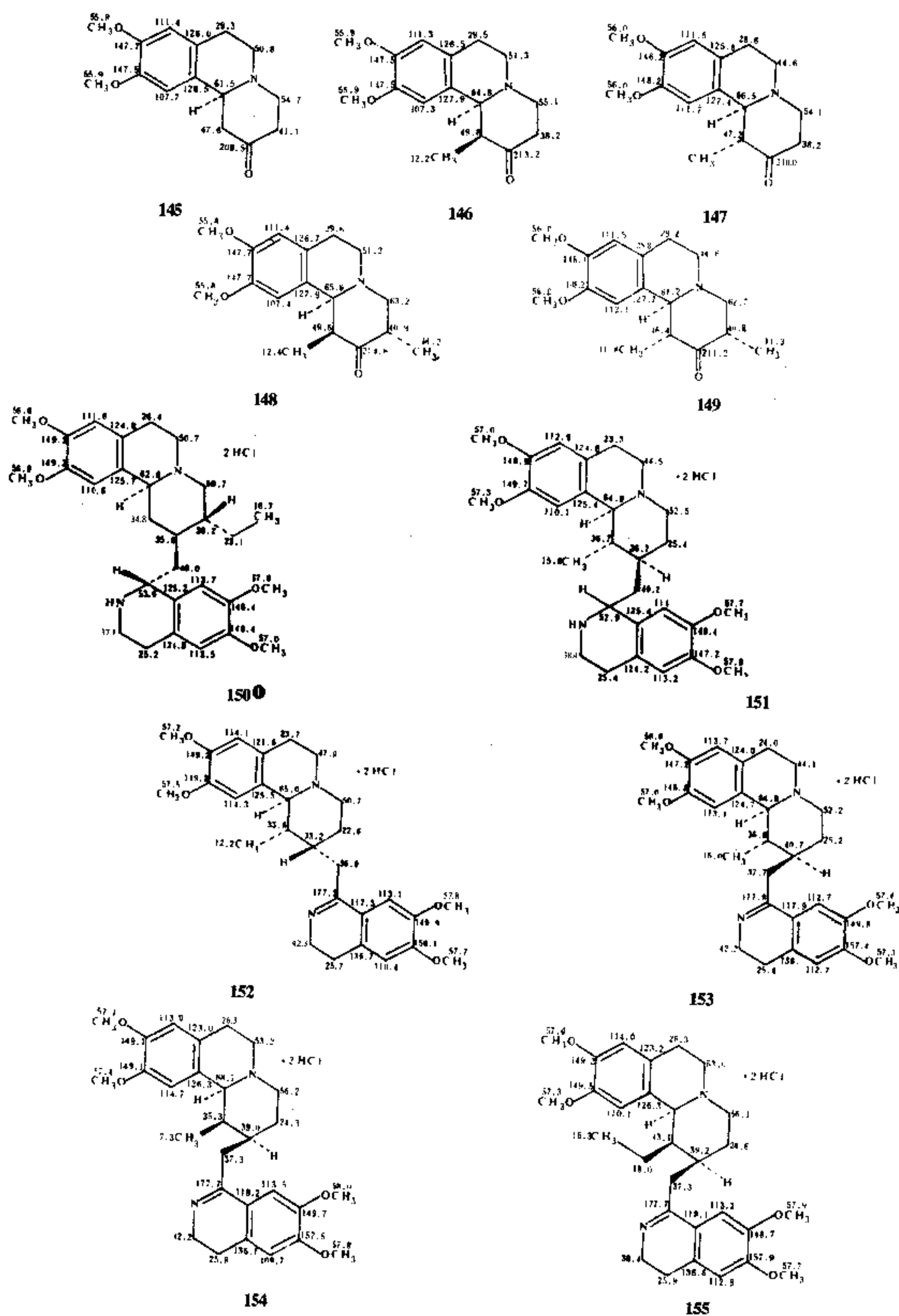

141


142


143


144

十、吐根碱类生物碱的^{13}C-NMR化学位移[65]

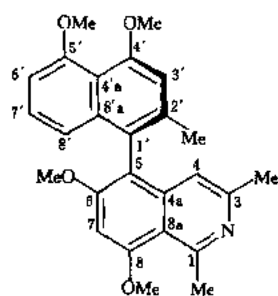


● 化合物150～155在D_2O中测定。

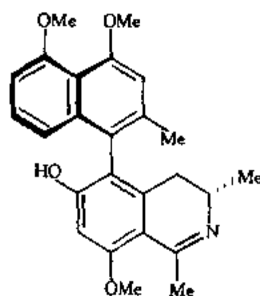
十一、苯基异喹啉类生物碱的^{13}C-NMR化学位移

表 20-17　几个异喹啉生物碱的^{13}C-NMR谱化学位移数据[174]

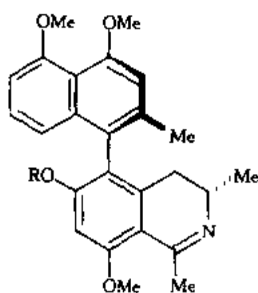
C \ 化合物	1	2	3	4	5	6	7
1	158.0	165.8	165.8	166.1	57.4	57.3	57.9
1-Me	27.8	23.5	23.5	26.8	22.1	22.1	22.8
2-Me					40.9	40.9	41.2
3	150.0	46.6	46.5	50.2	55.1	55.0	55.6
3-Me	23.4	18.1	18.0	20.5	20.6	21.1	20.5
4	114.5	32.3	32.2	31.5	38.8	39.4	37.9
4a	140	138.6	138.6	141.1	137.5	136.8	137.1
5	114	123.0	123.0	119.6	106.0	102.3	109.5
6	158.8	165.8	165.8	161.6	151.7	155.8	152.3
6-OMe	56.3			55.6		55.7	
7	94.2	100.3	100.3	93.8	102.2	112.1	116.9
8	160.2	164.1	164.1	159.9	150.2	150.4	155.8
8-OMe	55.5	54.7	54.7	55.5			59.9
8a	114.0	101.8	101.6	111.6	118.4	119.5	124.1
1′	124.0	126.2	126.5	123.9	116.6	119.8	119.7
2′	136.3	135.7	135.1	135.1	139.6	137.7	138.4
2′-Me	20.4	20.2	20.3	20.4	21.0	20.6	20.7
3′	109.1	109.1	109.2	108.9	108.6	108.9	109.1
4′	156.7	155.8	155.8	156.5	157.7	157.2	157.4
4′-OMe	56.4	56.2	56.2	56.5	56.0	56.2	56.3
4′a	116.2	116.1	116.1	116.3	116.4	116.5	116.4
5′	157.5	157.1	157.0	157.5	157.4	157.4	157.6
5′-OMe	56.5	56.2	56.1	56.4	56.3	56.4	56.4
6′	105.5	105.5	105.2	105.5	106.0	105.8	105.7
7′	126.4	126.3	126.1	126.5	127.7	127.9	127.4
8′	118.6	118.3	118.4	117.5	117.5	118.0	117.9
8′a	137.1	136.4	136.7	136.5	136.9	136.9	136.4



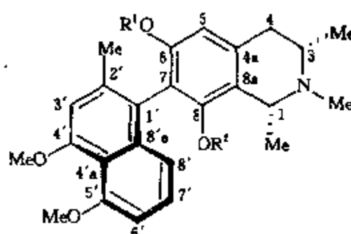
156



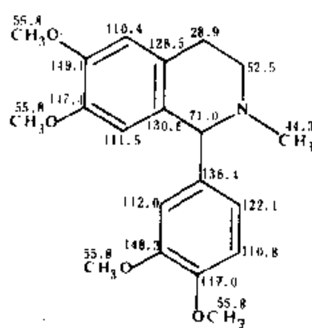
157



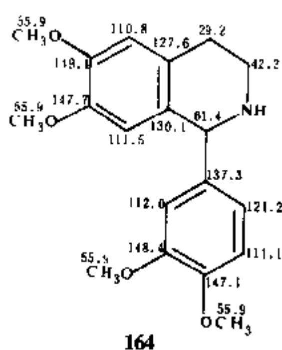
158. R = H
159. R = Me



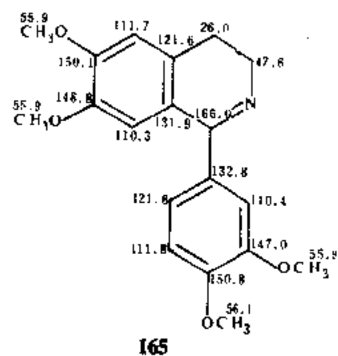
160. $R^1 = R^2 = H$
161. $R^1 = Me, R^2 = H$
162. $R^1 = H, R^2 = Me$



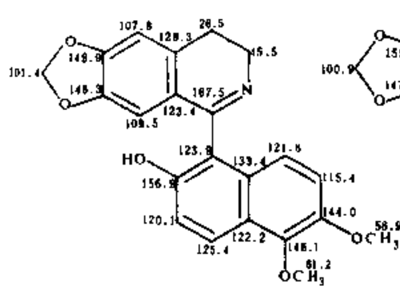
163



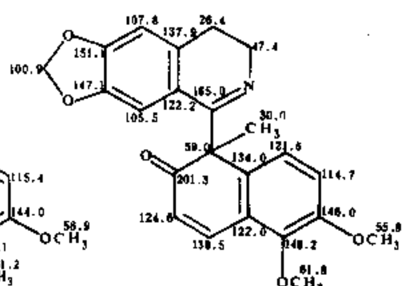
164



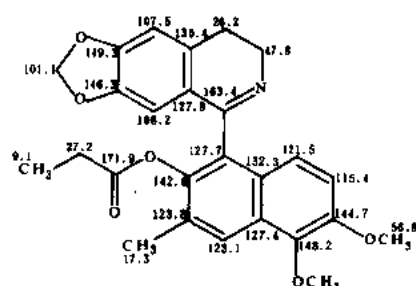
165



166

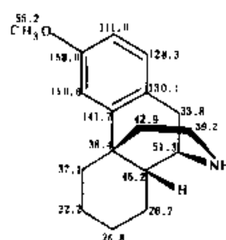


167

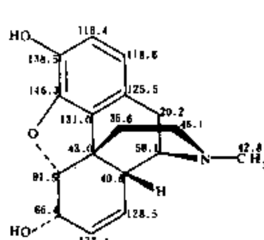


168

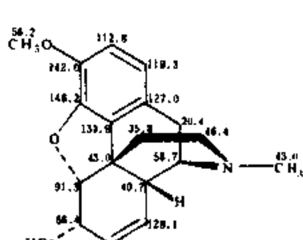
十二、吗啡烷类生物碱的^{13}C-NMR化学位移



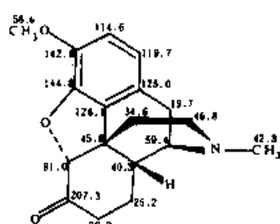
169[66]



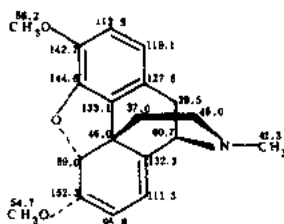
170[66]



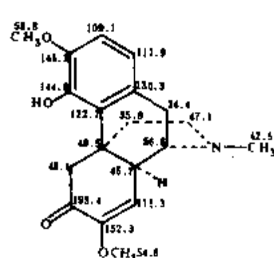
171[67]



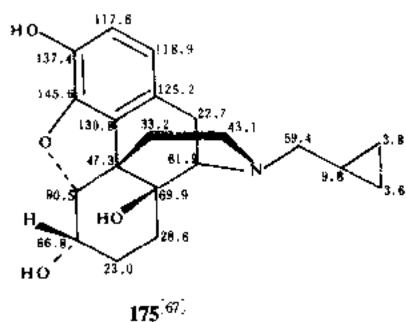
172[67]



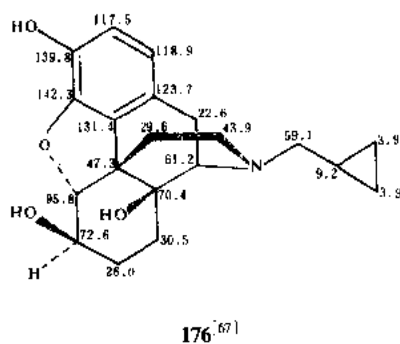
173[66]



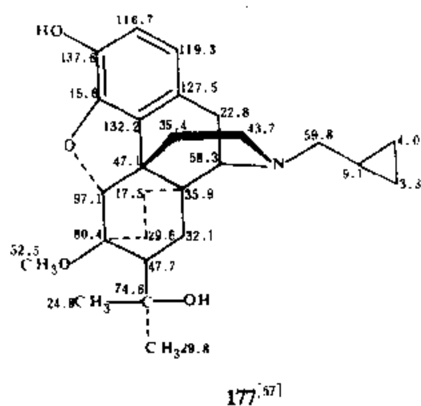
174[66]



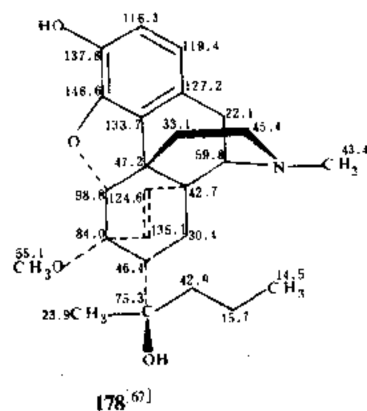
175[67]



176[67]

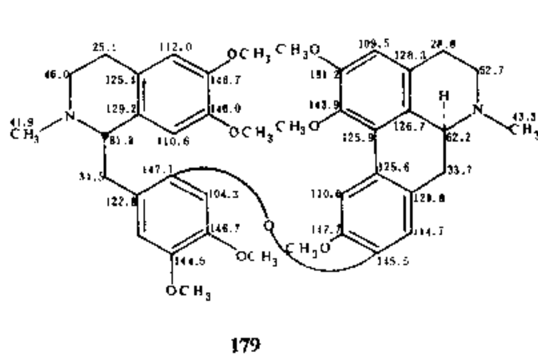


177[67]

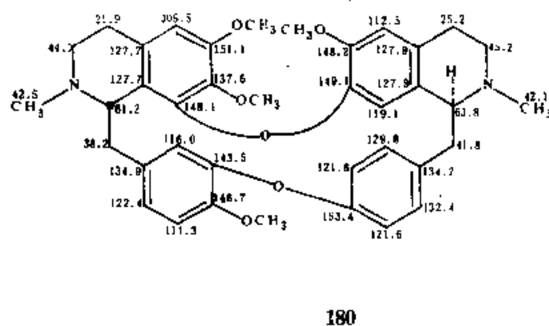


178[67]

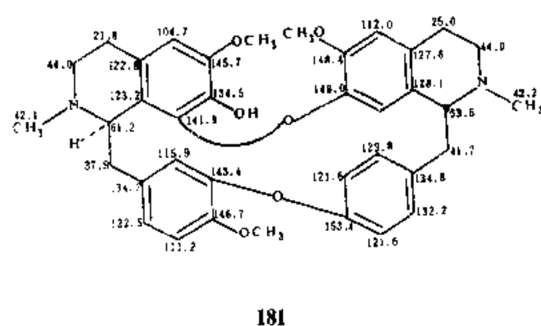
十三、双苄基异喹啉类生物碱的^{13}C-NMR 化学位移[68]



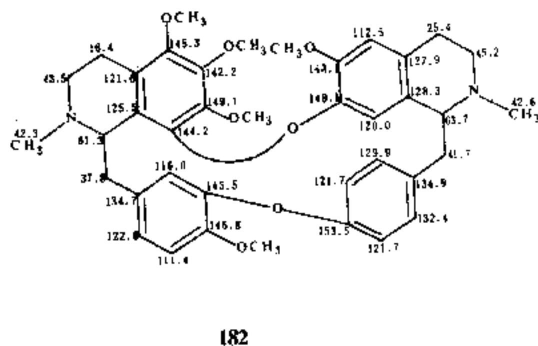
179



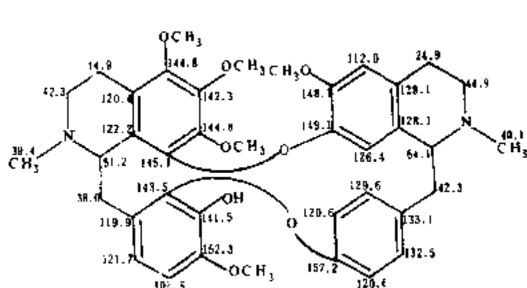
180



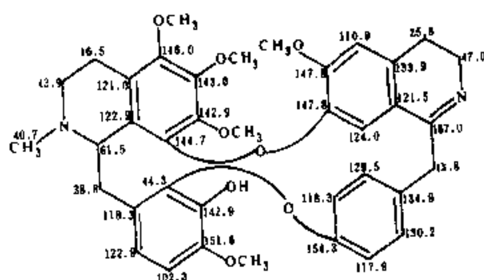
181



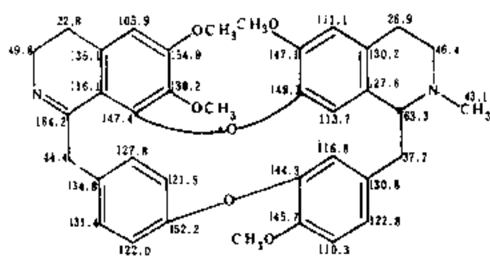
182



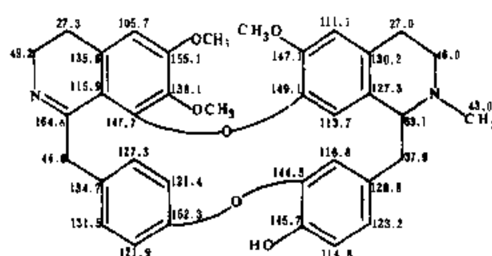
183



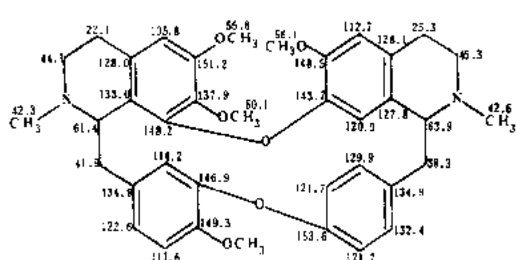
184



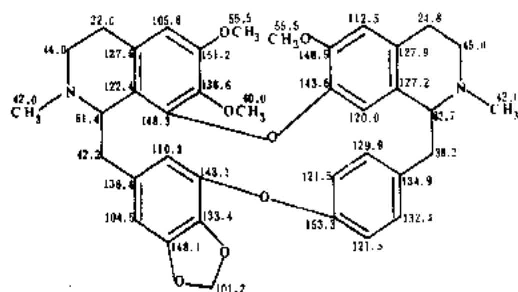
185



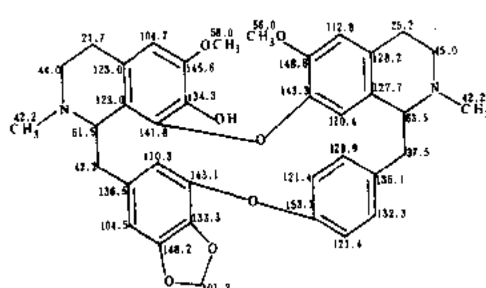
186



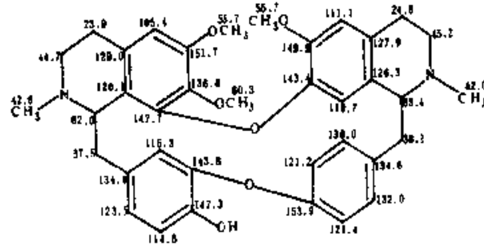
187



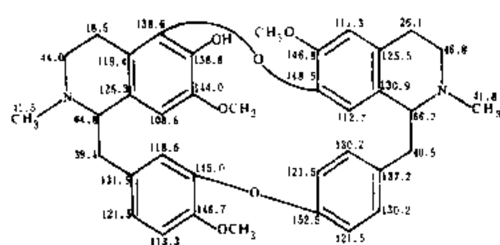
188



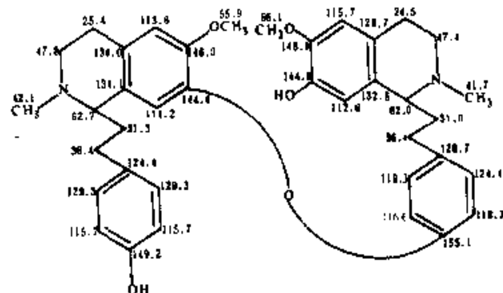
189



190



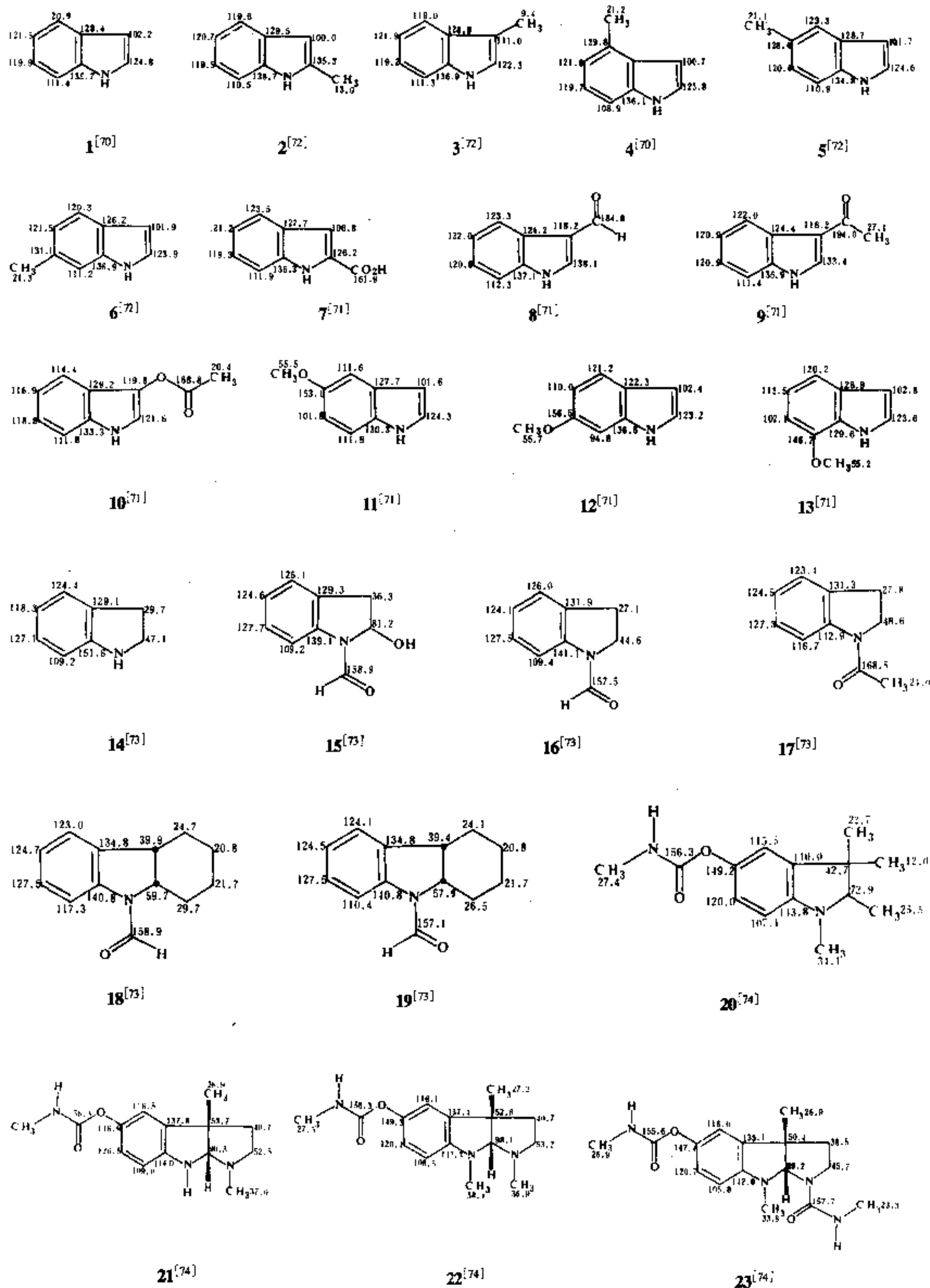
191

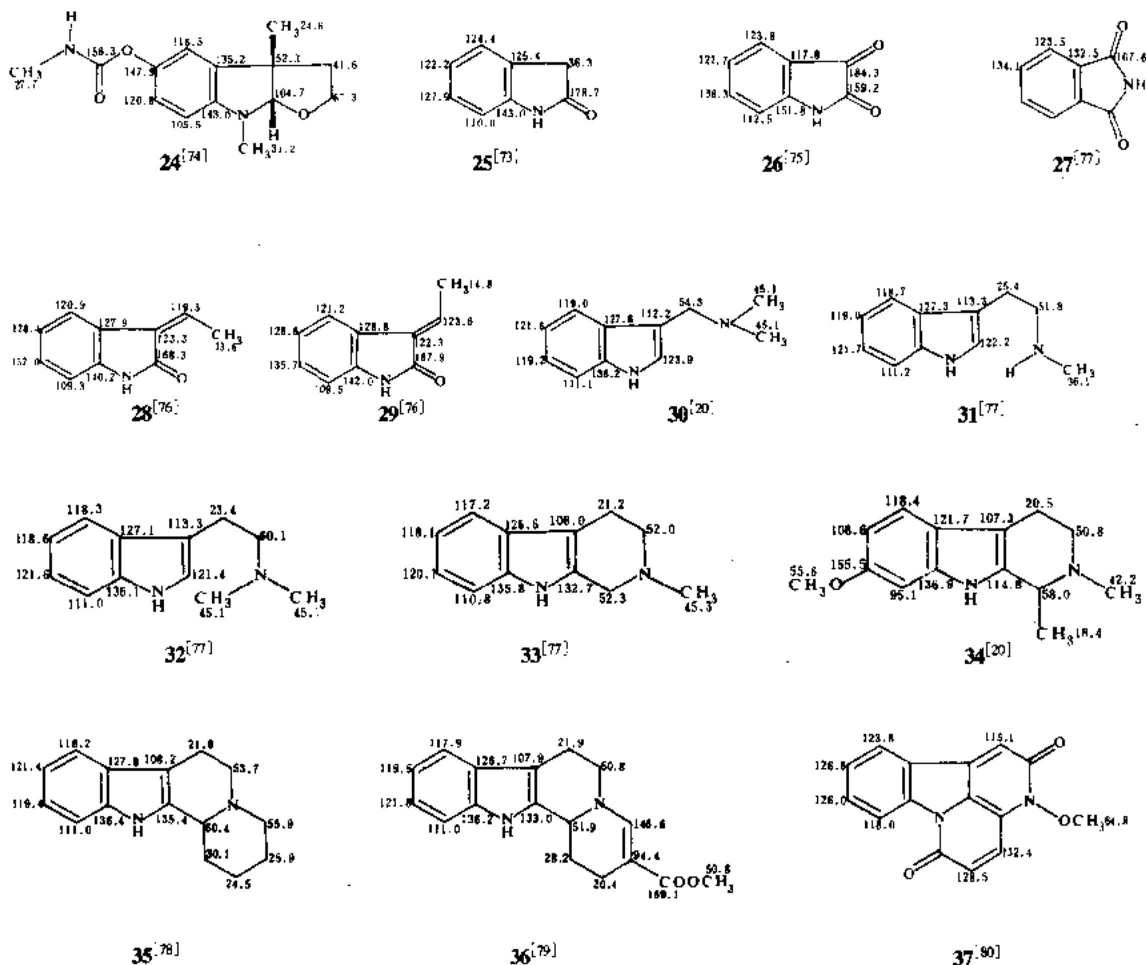


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第八节　吲哚类生物碱的¹³C-NMR 化学位移

一、简单吲哚类生物碱的¹³C-NMR 化学位移



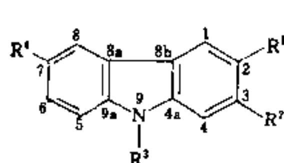


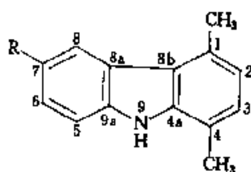
二、咔唑类生物碱的¹³C-NMR 化学位移

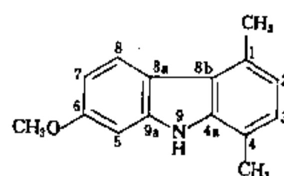
1. 一般咔唑类生物碱的¹³C-NMR 化学位移

表 20-18　咔唑类生物碱 38～46 的¹³C-NMR 化学位移数据[81]

C \ 化合物	38	39	40	41,42	43	44	45	46
1	120.1	120.2	119.8	130.9	131.0	129.4	130.6	129.9
2	118.6	118.7	128.2	121.0	121.3	119.1	120.4	121.0
3	125.6	125.7	135.6	126.2	126.8	125.3	126.0	125.2
4	111.0	109.0	110.8	117.1	117.3	117.2	117.0	116.7
4a	139.9	140.6	139.3	139.5	139.2	139.7	139.6	140.4
5	111.0	109.0	111.1	110.6	111.8	111.1	110.9	94.8
6	125.6	125.7	114.2	125.1	127.8	114.0	113.4	158.5
7	118.6	118.7	153.4	119.5	112.1	150.3	153.5	108.0
8	120.1	120.4	103.2	122.6	126.8	107.0	106.3	123.3
8a	122.6	122.0	121.7	124.6	126.7	123.9	124.8	118.6
8b	122.6	122.0	123.7	121.5	120.5	120.3	121.3	121.6
9a	139.9	140.6	135.6	138.8	137.9	133.8	134.4	138.8
其他碳		28.8	23.6～23.8	16.5	16.4	16.7	16.4	16.5
			29.8～30.4	20.5	20.3	20.1	20.2	20.3
			56.2				56.1	55.6







38. $R^1 = R^2 = R^3 = R^4 = H$

39. $R^1 = R^2 = R^4 = H, R^3 = CH_3$

40. $R^1 + R^2 = \leftarrow CH_2 \rightarrow_4$

$R^3 = H, R^4 = OCH_3$

41. R = H　**44**. R = OH

42. R = D　**45**. $R = OCH_3$

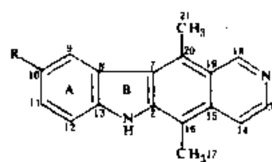
43. R = Br

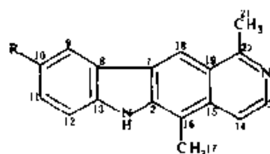
46

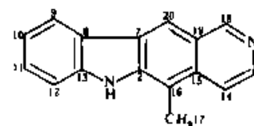
2. 吡啶咔唑生物碱^{13}C-NMR 化学位移

表 20-19　吡啶咔唑生物碱 47~53 的^{13}C-NMR 化学位移数据[81]

C \ 化合物	47	48	49	50	51	52	53
2	140.4	140.0	141.1	140.4	141.5	142.3	140.4
3	140.9	46.3	140.1	140.7	137.8	140.4	140.7
7	121.9	118.9	121.5	121.8	121.2	119.3	122.4
8	123.3	123.3	123.5	122.7	123.0	122.2	123.4
9	123.6	122.1	107.7	121.3	104.4	121.3	121.1
10	119.1	118.7	153.0	119.0	153.4	119.3	119.1
11	127.0	124.7	115.0	127.4	115.0	128.0	127.6
12	110.5	110.9	111.0	110.8	111.5	111.0	110.8
13	142.6	140.6	137.1	142.5	137.1	142.7	142.5
14	115.8	22.9	115.6	115.3	115.0	119.3	115.8
15	132.3	132.4	132.1	132.3	132.1	134.0	132.1
16	107.9	113.9	107.7	110.8	111.0	103.5	110.8
17	11.8	12.2	11.8	12.3	12.3		12.0
18	152.9	157.7	149.5	114.7	116.6	152.9	153.1
19	123.3	129.9	128.1	124.7	125.1	126.3	125.2
20	123.0	122.1	123.3	158.6	158.4	119.3	116.8
21	14.2	14.4	14.1	22.9	22.3		
其他碳			55.6		55.6		







47. R = H

48. R = H, 3, 14-H

49. $R = OCH_3$

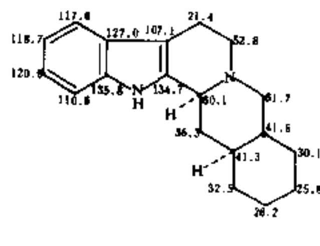
50. R = H

51. $R = OCH_3$

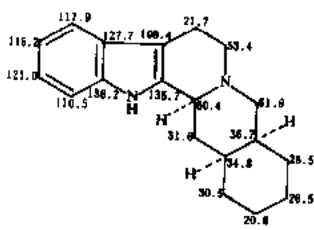
52

53

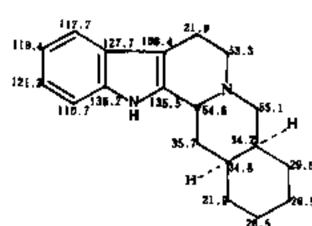
三、育亨宾类生物碱的^{13}C-NMR 化学位移[79]



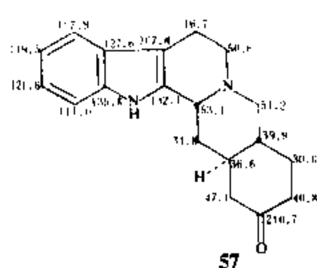
54



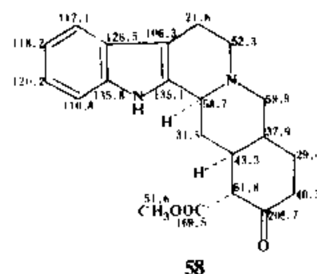
55



56



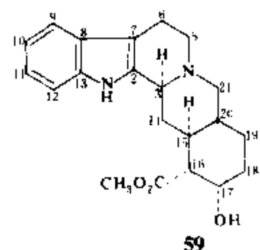
57



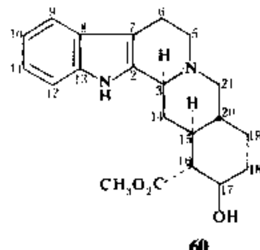
58

表 20-20　育亨宾生物碱 59～68 的^{13}C-NMR 化学位移数据

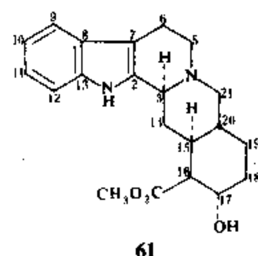
C \ 化合物	59	60	61	62	63	64	65	66	67	68
2	134.3	134.0	135.8	134.0	134.3	134.4	131.7	130.2	131.3	131.3
3	59.8	59.0	60.5	53.7	60.1	60.1	53.7	53.6	53.5	53.4
5	52.1	52.3	52.6	50.7	53.2	52.8	50.8	51.1	50.8	50.6
6	21.5	21.3	21.6	16.4	21.7	21.3	16.5	16.7	16.4	16.3
7	107.5	107.4	106.3	105.9	108.1	107.1	107.3	107.7	107.5	106.8
8	127.0	126.9	127.0	127.2	127.1	126.8	127.2	121.9	127.3	127.0
9	117.7	117.7	117.5	117.2	117.9	117.5	117.6	118.2	117.6	117.3
10	118.8	118.8	118.4	119.1	119.1	118.6	118.9	108.7	119.1	118.7
11	120.8	120.9	120.4	120.1	121.1	120.5	121.0	155.8	121.2	120.8
12	110.6	110.7	111.1	111.1	110.6	110.6	110.8	95.0	110.7	110.8
13	135.8	135.8	136.1	135.5	135.7	135.8	135.6	136.1	135.5	135.6
14	33.8	33.8	33.6	32.2	27.6	31.0	23.6	24.1	23.7	23.5
15	35.4	41.6	34.7	32.4	37.9	37.4	32.5	32.2	31.9	32.5
16	52.6	57.1	51.1	52.4	54.6	50.6	54.1	51.6	52.1	49.9
17	66.9	71.6	65.9	66.6	66.0	66.7	65.7	77.8	68.3	73.8
18	31.4	33.5	28.2	30.9	33.2	30.2	33.5	77.7	76.9	72.9
19	23.1	27.5	23.5	23.0	24.5	24.8	23.9	29.6	29.1	32.5
20	40.2	39.1	36.5	39.5	36.4	32.0	35.6	33.8	33.7	34.1
21	61.0	60.5	62.0	51.5	60.4	59.6	49.4	48.8	48.7	48.6
C=O	175.1	175.0	172.7	172.9	174.4	174.0	174.7	172.5	172.8	171.8
OCH_3	51.7	51.6	51.1	51.2	51.8	51.5	51.7	51.6	51.7	51.7



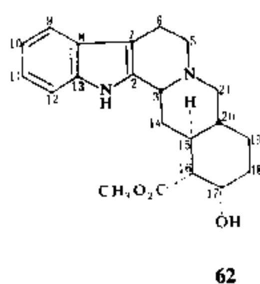
59



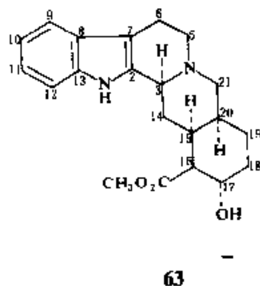
60



61

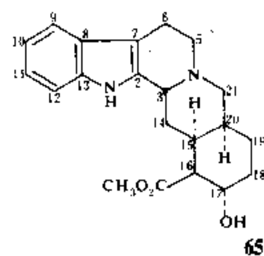


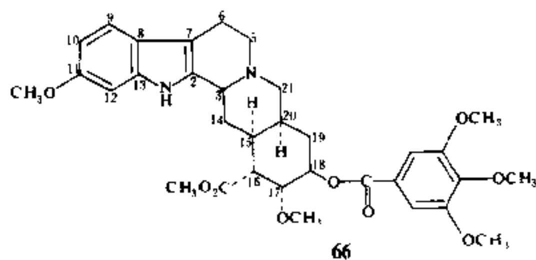
62

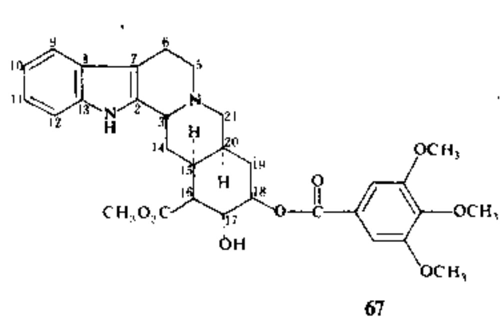


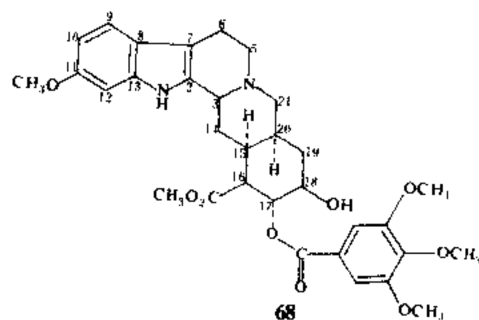
63

64







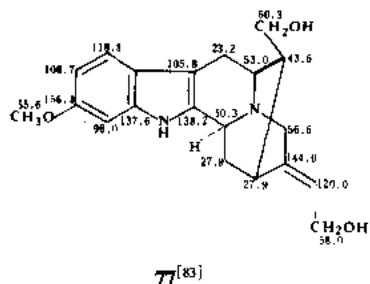


四、蛇根碱类生物碱的^{13}C-NMR 化学位移

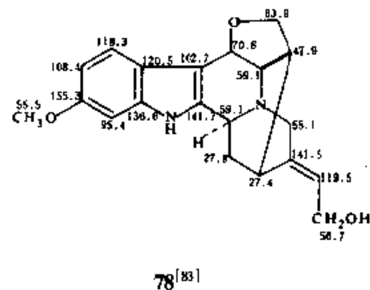
表 20-21　蛇根碱类生物碱 69 ~ 73 的^{13}C-NMR 化学位移数据[79]

C \ 化合物	69	70	71	72	73	C \ 化合物	69	70	71	72	73
2	134.0	132.4	134.4	134.3	132.8	14	32.1	31.2	34.2	32.5	30.6
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

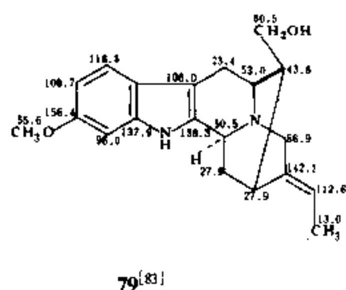
五、沃洛亭类生物碱的^{13}C-NMR 化学位移



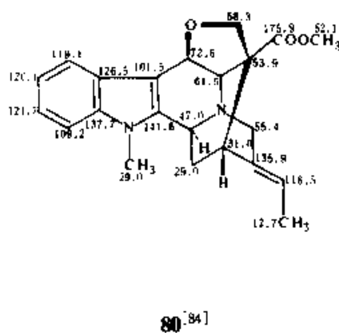
77[83]



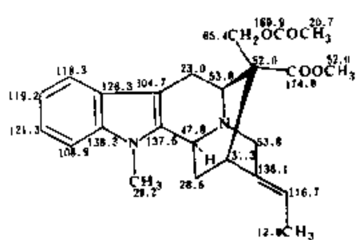
78[83]



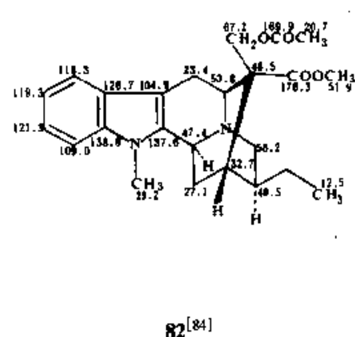
79[83]



80[84]

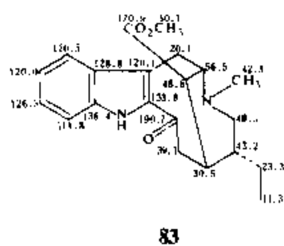


81[84]

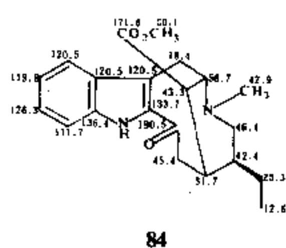


82[84]

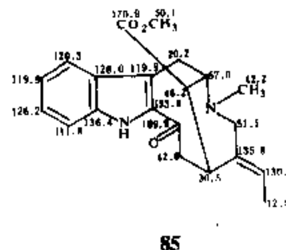
六、波里芬类生物碱的^{13}C-NMR 化学位移



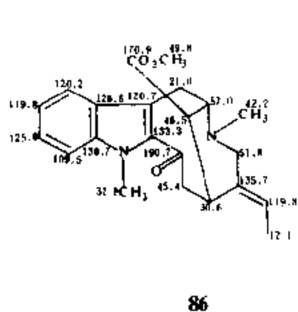
83



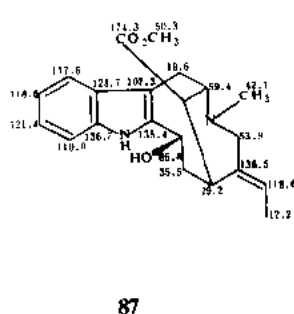
84



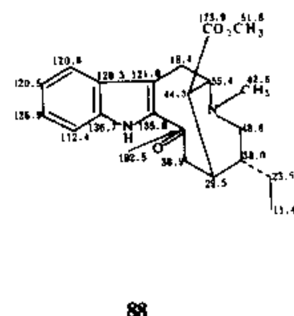
85



86



87



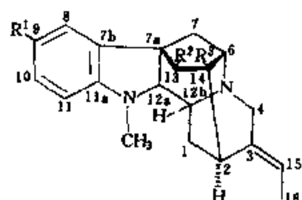
88

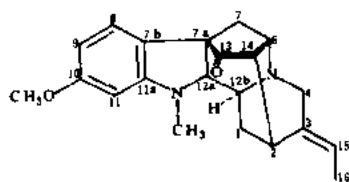
七、阿马林类生物碱的^{13}C-NMR化学位移

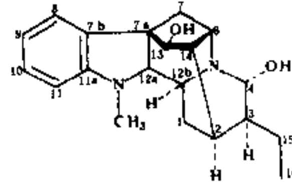
表 20-22 阿马林类生物碱 89 ~ 93 的^{13}C-NMR 化学位移数据[86]

C \ 化合物	89	90	91	92	93	C \ 化合物	89	90	91	92	93
1	29.2	29.4	21.4	31.5	31.6	11a	147.7	147.8	153.8	155.1	154.0
2	27.9	27.8	29.6	28.5	28.4	12a	79.6	79.6	74.4	78.4	79.4
3	138.6	139.3	135.6	137.3	42.2	12b	49.0(b)	49.3(b)	52.7	50.1(b)	44.6(b)
4	54.6	55.2	54.7	55.7	87.6	13	76.0	79.1	73.9	214.0	76.3
6	55.8(b)①	55.9(b)	61.1	53.1(b)	52.5(b)	14	51.9	50.1	59.6	50.3(b)	48.7(b)
7	34.9	36.1	35.0	35.3	35.3	15	114.2	114.3	116.1	115.7	25.5
7a	54.9	53.6	56.5	57.8	55.5	16	12.5	12.8	12.3	12.9	12.3
7b	134.4	133.3	129.7	121.6	134.5	NCH_3	34.8	35.1	33.8	34.2	34.3
8	110.2	110.0	124.2	122.5	123.1	$ArOCH_3$	55.6	55.5		55.3	
9	153.0	153.0	118.5	103.8	118.5	C＝O,酯		169.9	172.8		
10	111.4	111.1	127.6	160.1	126.7	CH_3		21.1	51.1		
11	109.2	109.6	108.4	97.5	109.1						

① (b)表示可以互换的数据。



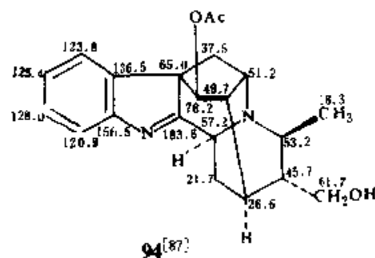




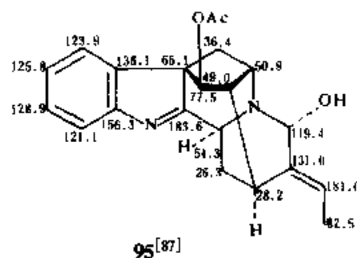
89. $R^1 = OCH_3, R^2 = OH, R^3 = H$
90. $R^1 = OCH_3, R^2 = OAc, R^3 = H$
91. $R^1 = H, R^2 = OH, R^3 = COOCH_3$

92

93



94[87]



95[87]

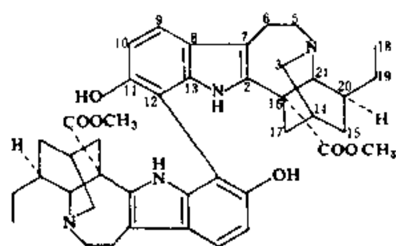
八、长春花碱型生物碱的^{13}C-NMR化学位移

表 20-23 长春花碱型生物碱 96 ~ 104 的^{13}C-NMR 化学位移数据[88]

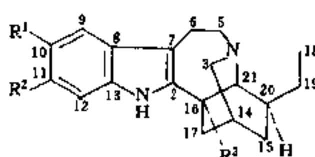
C \ 化合物	96	97	98	99	100	101	102	103	104
2	136.2	136.0	137.3	136.3	141.9	142.9	140.7	135.8	136.0
3	51.1	51.5	51.7	51.4	49.9	50.0	49.8	51.3	49.4
5	53.1	53.0	53.1	53.1	54.2	54.2	54.1	52.2	52.9
6	22.2	22.0	22.2	22.2	20.7	20.7	20.8	21.4	21.4
7	111.0	110.0	110.0	110.0	109.2	109.1	108.9	109.7	110.4
8	123.4	128.0	129.1	123.2	129.8	129.7	124.3	128.4	128.6
9	120.2	117.9	100.7	119.0	118.0	100.3	118.5	118.4	117.7
10	110.0	118.7	154.0	108.9	119.1	153.9	108.4	119.3	119.0

续表

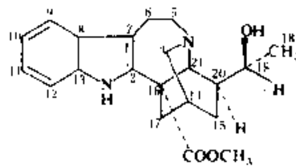
C \ 化合物	96	97	98	99	100	101	102	103	104
11	149.8	121.4	111.9	156.5	120.9	110.8	155.8	122.0	121.3
12	100.0	109.7	111.1	94.3	110.2	110.6	94.4	110.4	110.1
13	133.8	135.0	130.6	135.3	134.7	130.0	135.4	135.6	134.6
14	27.2	27.3	27.3	27.4	26.6	26.5	26.6	26.7	30.7
15	31.9	31.9	32.0	32.1	32.2	32.0	32.2	23.0	123.2
16	55.0	54.9	55.0	55.1	42.1	42.0	42.0	54.2	55.3
17	36.1	36.4	36.5	36.4	34.2	34.2	34.2	36.9	38.4
18	11.6	11.9	11.7	11.7	11.9	11.9	11.9	20.4	10.7
19	26.7	26.7	26.7	26.7	27.9	27.8	27.8	71.3	26.2
20	39.0	39.0	39.1	39.2	41.5	41.5	41.4	39.5	148.8
21	58.2	57.2	57.6	57.6	57.6	57.5	57.8	59.7	61.7
C = O	175.0	175.0	175.6	175.9	—			174.5	173.5
OCH_3	52.3	52.3	52.7	52.5	—			52.9	52.0
Ar-OCH_3	—	—	55.7	55.7	—	56.0	55.8	—	—



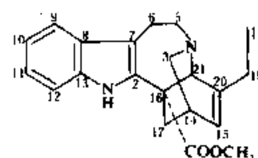
96



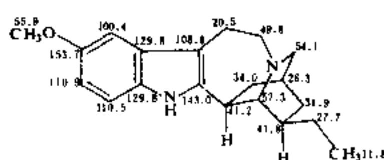
97. $R^1 = R^2 = H, R^3 = COOCH_3$
98. $R^1 = OCH_3, R^2 = H, R^3 = COOCH_3$
99. $R^1 = H, R^2 = OCH_3, R^3 = COOCH_3$
100. $R^1 = R^2 = R^3 = H$
101. $R^1 = OCH_3, R^2 = R^3 = H$
102. $R^1 = R^3 = H, R^2 = OCH_3$



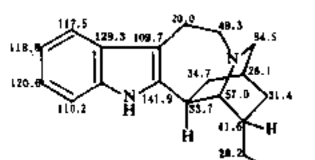
103



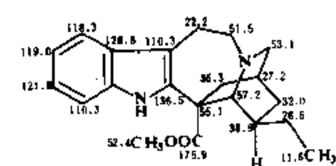
104



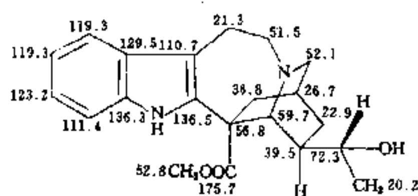
105



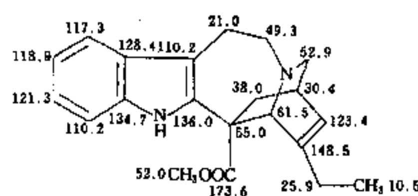
106



107



108



109

九、白坚木碱型生物碱的^{13}C-NMR化学位移

110[90]

111[91]

112[91]

113[91]

114[92]

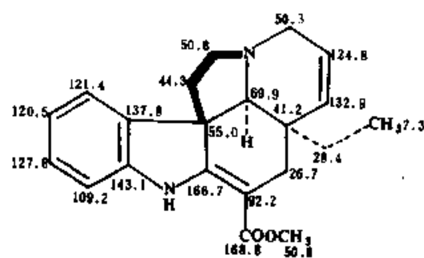
115[93]

116[93]

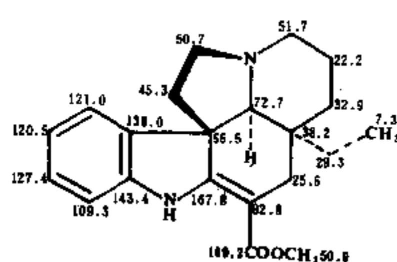
117[94]

118[94]

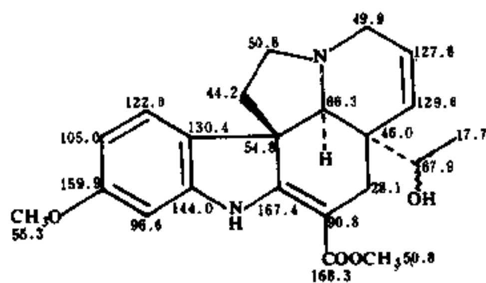
119[95]



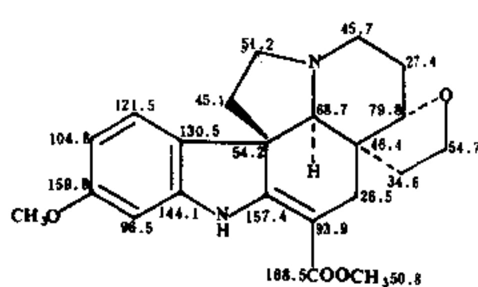
120[96]



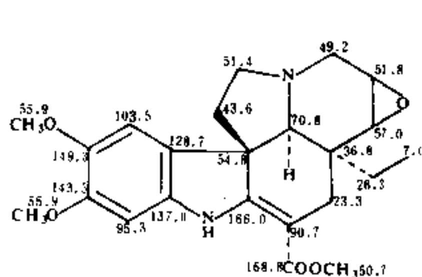
121[96]



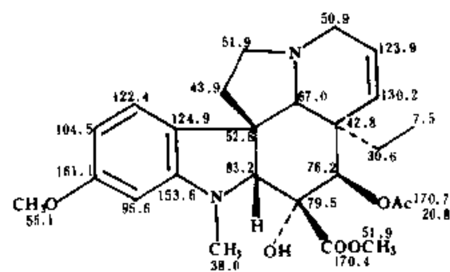
122[96]



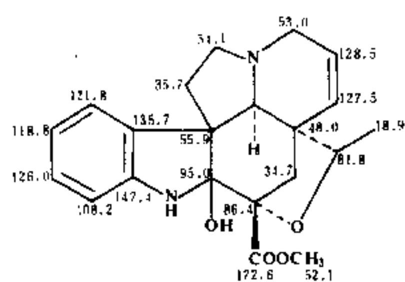
123[96]



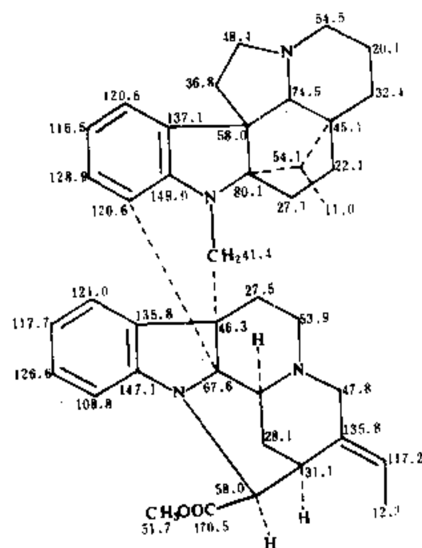
124[96]



125[96]



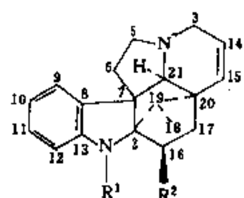
126[97]



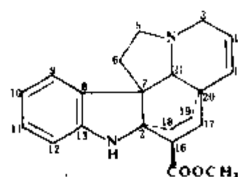
127[93]

表 20-24　白坚木碱型生物碱 128～133 的^{13}C-NMR 化学位移数据[98]

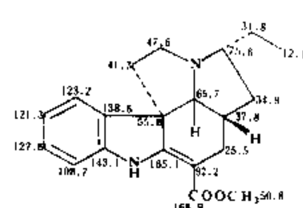
C \ 化合物	128	129	130	131	132	133	C \ 化合物	128	129	130	131	132	133
2	81.4	84.4	32.2	80.5	80.6	66.5	14	128.5	127.7	127.6	128.2	20.7	126.5
3	58.0	58.0	58.2	57.4	55.0	49.0	15	130.7	130.8	132.0	130.6	31.2	132.5
5	50.3	50.0	50.0	50.1	48.1	50.0	16	39.2	37.0	36.8	39.4	40.2	43.4
6	36.3	36.0	36.8	35.0	37.3	36.4	17	29.1	28.0	30.0	31.9	29.0	29.6
7	59.8	58.8	59.0	60.7	60.3	56.1	18	7.4	9.0	7.4	7.8	7.5	31.6
8	139.8	135.8	138.6	135.7	140.1	139.5	19	48.4	47.0	46.6	44.8	51.0	34.0
9	123.6	123.0	123.8	123.1	123.6	121.1	20	46.2	45.6	48.0	47.8	44.5	35.0
10	121.0	117.8	120.8	118.9	121.1	119.0	21	78.0	77.0	78.0	76.4	78.8	66.8
11	127.2	127.7	127.1	126.9	127.2	126.8	CO	174.2	174.0	63.6	174.5	175.0	173.7
12	112.0	105.6	110.8	109.0	112.7	110.9	OCH_3	51.8	52.0		51.7	52.0	51.6
13	149.4	150.2	148.6	148.7	149.5	149.0	NCH_3		30.0				



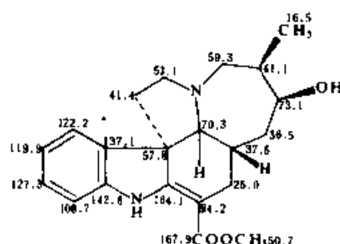
128. $R^1 = H, R^2 = CO_2CH_3$
129. $R^1 = CH_3, R^2 = CO_2CH_3$
130. $R^1 = H, R^2 = CH_2OH$
131. 16-表-
132. 14,15-二氢-



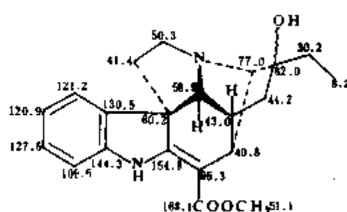
133



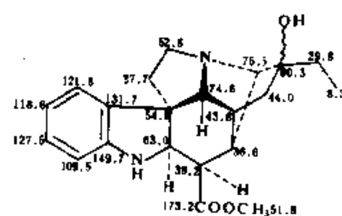
134[99]



135[99]

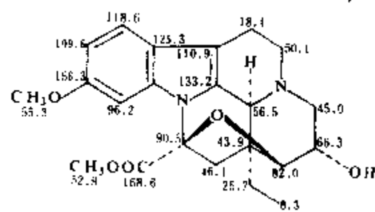


136[100]

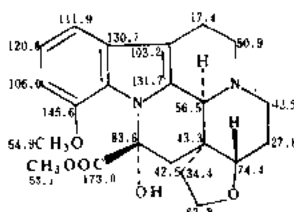


137[100]

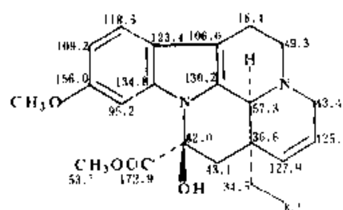
十、长春胺类生物碱的^{13}C-NMR 化学位移



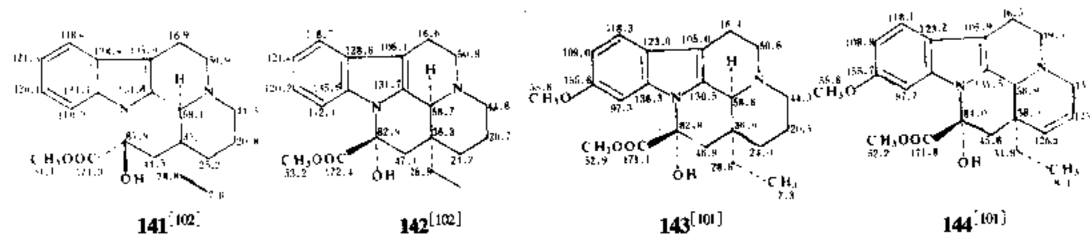
138[101]



139[102]

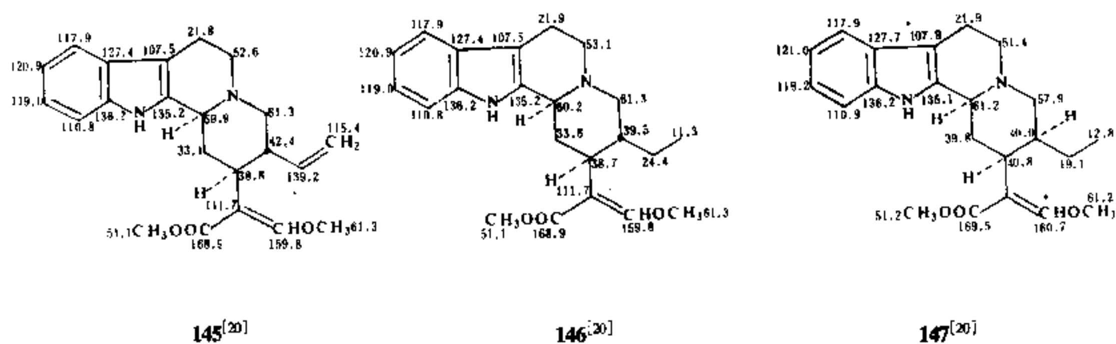


140[102]

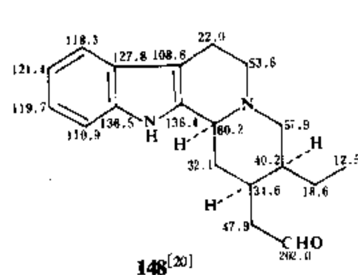


141[102]　142[102]　143[101]　144[101]

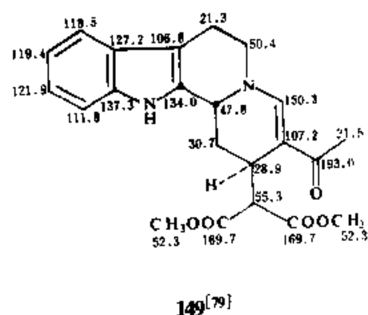
十一、柯楠碱型生物碱的^{13}C-NMR化学位移



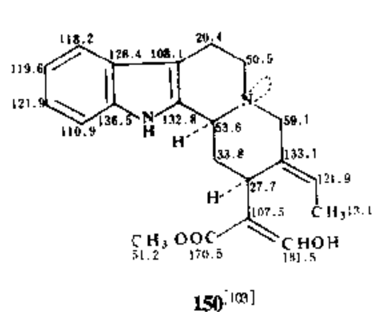
145[20]　146[20]　147[20]



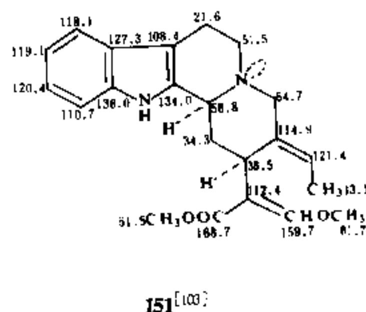
148[20]



149[79]



150[103]



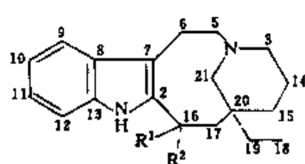
151[103]

十二、长春蔓啶碱型生物碱的^{13}C-NMR化学位移

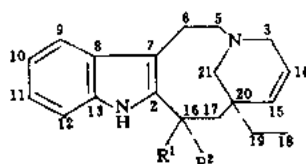
表 20-25 长春蔓啶碱型生物碱 152～172 的^{13}C-NMR 化学位移数据[104]①

C \ 化合物	152	153	154	155	156	157	158	159	160	161
2	139.7	133.7	135.2	141.2	134.4	135.1	139.2	134.2	138.1	
3	54.9	53.8	55.0	55.1	52.0	54.4	53.5	52.5	47.6	53.1
5	53.2	54.0	52.7	53.0	53.7	51.5	53.8	53.2	51.7	53.9
6	21.7	26.2	21.8	22.0	26.0	21.3	26.1	26.0	22.2	26.1
7	108.3	111.5	109.4	109.1	111.5	109.1	109.5	110.9	109.1	112.2
8	128.6	127.6	127.7	127.8	127.8	127.6	128.5	127.5	128.1	
9	117.1	117.9	117.4	117.2	118.0	117.3	117.6	117.7	117.3	118.1
10	118.4	118.7	118.5	118.4	118.7	118.5	118.5	118.5	118.5	118.6
11	119.9	121.4	120.6	120.1	121.3	120.6	120.3	111.0	120.4	121.4
12	109.9	110.6	110.5	110.3	110.5	110.4	109.8	110.3	110.3	110.4
13	134.5	135.7	134.9	134.8	135.7	134.7	135.2	135.5	134.8	
14	22.6	23.6	22.3	22.5	127.0	124.6	35.3	34.3	34.0	34.4
15	33.4	37.3	33.9	34.1	132.9	135.4	122.3	121.5	124.7	122.0
16	22.4	40.9	37.8	33.7	39.1	38.1	22.4	38.3	36.6	72.8
17	34.7	42.8	38.6	35.8	43.4	44.1	34.1	37.5	36.2	41.5
18	7.8	7.3	7.4	7.6	7.7	8.3	12.6	12.3	12.3	12.6
19	32.0	35.6	30.6	31.0	33.1	29.3	27.6	27.4	27.3	27.5
20	36.9	35.6	37.9	37.6	39.5	40.9	140.4	140.8		141.9
21	56.6	60.8	56.7	56.8	58.6	51.5	55.1	54.9	57.1	54.9
C＝O		175.6	176.2		175.6	175.6		175.3		
OCH_3		51.9	52.0		51.8	52.0		51.8		55.7
OCH_2				67.4					66.6	
C \ 化合物	**162**	**163**	**165**	**166**	**167**	**168**	**169**	**170**	**171**	**172**
2	138.4		138.4	139.0	133.8	139.4	133.7	135.0	138.5	
3	47.0	47.3	51.4	48.4	51.2	51.7	55.8	50.6	50.6	50.9
5	51.2	51.3	52.2	52.8	51.8	53.2	54.1	52.5	52.3	52.0
6	21.7	21.7	26.0	21.5	26.4	24.1	126.5	22.1	22.7	22.4
7	109.5	109.0	109.6	108.2	111.8	108.7	111.4	109.5	108.0	109.2
8	127.9	128.4	128.3	127.6	127.6	128.8	127.6	127.8	127.4	127.7
9	117.5	117.5	117.6	116.7	118.1	117.3	118.0	117.4	116.8	117.5
10	118.6	118.5	118.6	117.5	118.8	118.5	118.7	118.6	118.4	119.0
11	120.9	120.8	120.5	119.3	121.4	120.1	121.2	120.7	120.4	121.4
12	110.6	110.4	109.8	110.2	110.5	109.8	110.5	110.5	110.8	111.1
13	135.0			135.2	135.7	134.7	135.6	135.0	135.2	134.0
14	34.1	33.4	35.0	35.3	34.8	33.8	31.1	32.8	30.1	30.5
15	124.0	124.4	31.2	36.0	31.0	37.6	39.0	36.7	40.4	39.5
16	39.3	75.8	21.3	38.5	37.5	23.3	42.0	39.0	22.7	39.3
17	39.1	41.8	33.7	34.1	38.5	31.9	40.3	36.3	31.5	36.1
18	12.3	12.3	11.7	12.2	11.7	11.4	11.4	11.3	6.9	6.9
19	27.3	27.3	28.7	28.0	28.6	27.5	27.7	27.3	32.3	32.6
20	138.4	138.2	32.8	32.6	32.1	32.9	36.1	33.1	71.6	71.2
21	57.5	57.5	58.7	56.3	58.9	61.2	60.6	61.3	65.8	66.1
C＝O	175.8				175.3		175.4	176.1		175.2
OCH_3	52.2	57.4			52.0		52.0	52.1		52.2
OCH_2				65.2						

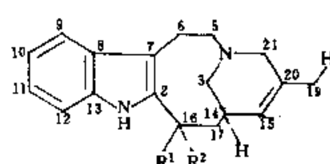
① 化合物 152～172 在$(CD_3)_2SO$中测定。



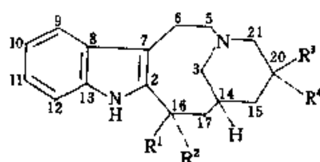
152. $R^1 = R^2 = H$
153. $R^1 = H, R^2 = CO_2CH_3$
154. $R^1 = CO_2CH_3, R^2 = H$
155. $R^1 = CH_2OH, R^2 = H$



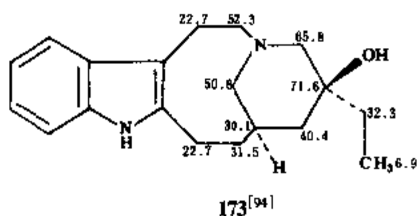
156. $R^1 = H, R^2 = CO_2CH_3$
157. $R^1 = CO_2CH_3, R^2 = H$



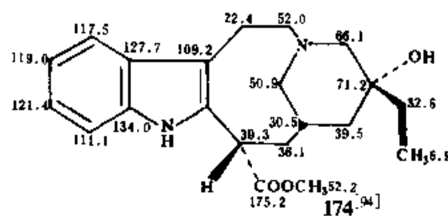
158. $R^1 = R^2 = H$
159. $R^1 = H, R^2 = CO_2CH_3$
160. $R^1 = CH_2OH, R^2 = H$
161. $R^1 = H, R^2 = OCH_3$
162. $R^1 = CO_2CH_3, R^2 = H$
163. $R^1 = OCH_3, R^2 = H$
164. $R^1 = H, R^2 = CH_2OH$



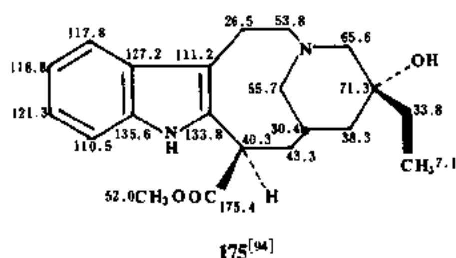
165. $R^1 = R^2 = R^4 = H, R^3 = CH_2CH_3$
166. $R^1 = CH_2OH, R^2 = R^4 = H, R^3 = CH_2CH_3$
167. $R^1 = R^4 = H, R^2 = CO_2CH_3, R^3 = CH_2CH_3$
168. $R^1 = R^2 = R^3 = H, R^4 = CH_2CH_3$
169. $R^1 = R^3 = H, R^2 = CO_2CH_3, R^4 = CH_2CH_3$
170. $R^1 = CO_2CH_3, R^2 = R^3 = H, R^4 = CH_2CH_3$
171. $R^1 = R^2 = H, R^3 = OH, R^4 = CH_2CH_3$
172. $R^1 = CO_2CH_3, R^2 = H, R^3 = OH, R^4 = CH_2CH_3$



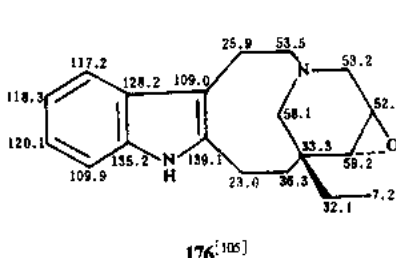
173[94]



174[94]

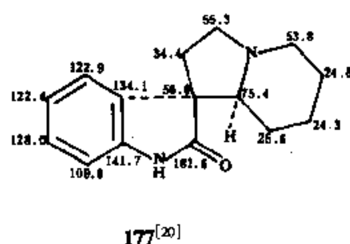


175[94]

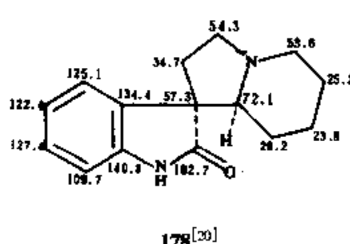


176[105]

十三、氧化吲哚生物碱的^{13}C-NMR化学位移



177[20]



178[20]

179[20]

180[20]

181[20]

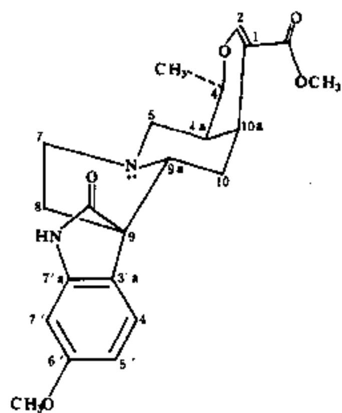
182[83]

183[83]

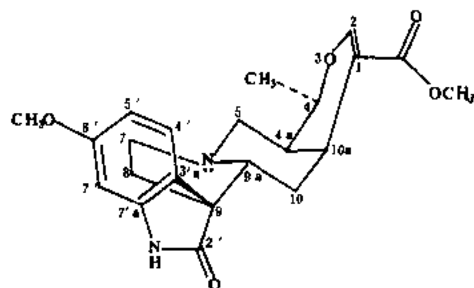
184[92]

表 20-26 氧化吲哚生物碱 185 ~ 190 的 ^{13}C-NMR 化学位移数据[106]

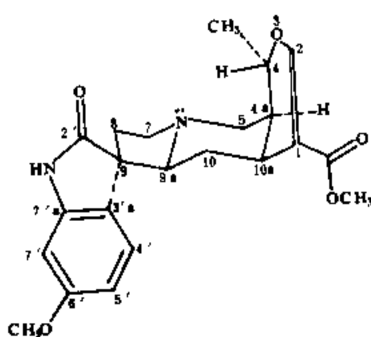
C \ 化合物	185	186	187	188	189	190	C \ 化合物	185	186	187	188	189	190
1	104.9	105	107.5	109.6	109.1	109.8	4′	125.3	123.0	123.3	124.3	117.8	119.4
2	153.5	153.5	154.5	154.9	154.9	154.8	5′	106.8	107.6	109.1	111.1	106.1	106.6
4	74.6	74.6	72.1	72.0	72.0	71.1	6′	159.6	159.8	159.7	159.6	152.2	152.1
4a	36.8	36.5	37.9	37.8	38.1	38.0	7′	96.6	96.7	96.8	102.7	133.9	132.9
5	53.7	54.6	55.0	54.0	54.6	53.9	7′a	141.5	142.2	141.8	140.2	132.5	133.7
7	53.2	53.2	53.6	53.5	53.3	53.4	C = O	167.3	167.3	167.4	167.3	167.4	167.4
8	34.8	34.2	34.6	36.6	33.7	35.1	$COCH_3$	50.7	50.3	50.7	50.8	50.6	50.8
9	56.0	55.3	55.4	56.6	55.9	57.1	6′-OCH_3	55.3	55.3	55.7	55.5	56.2	55.9
9a	67.2	70.1	74.3	72.3	74.0	72.1	7′-OCH_3	—	—	—	—	60.5	60.7
10	27.0	26.2	29.5	30.1	29.3	30.2	4′-CH_3	18.4	18.5	18.9	18.5	18.6	18.4
10a	24.8	25.1	31.0	30.4	30.8	30.4	N CO	—	—	—	170.5	—	—
2′	182.0	182.5	181.5	180.7	180.8	180.8							
3′a	125.4	125.0	125.1	123.9	126.5	126.9	N—$COCH_3$	—	—	—	25.6	—	—



185



186



187

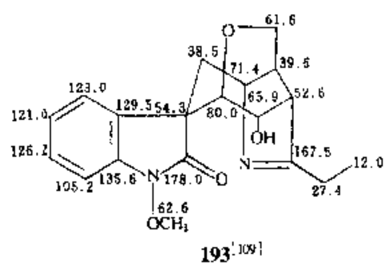
188

189

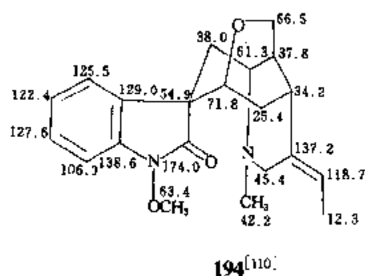
190

191[107]

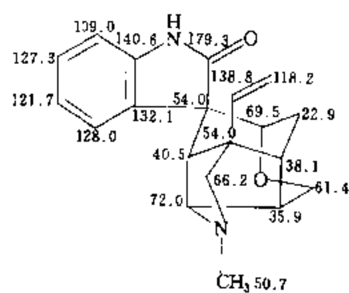
192[108]



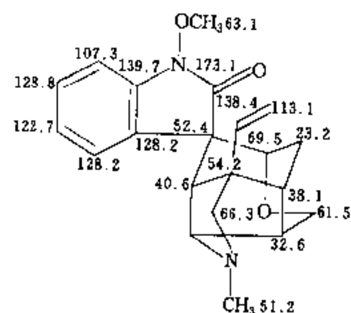
193[109]



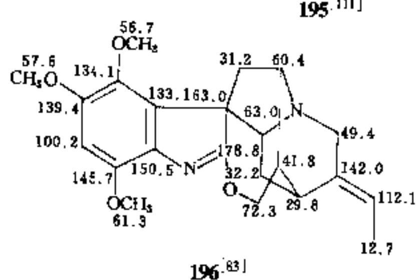
194[110]



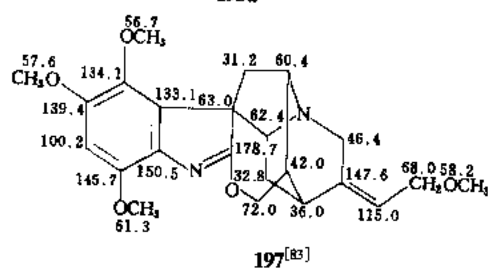
195[111]



195a[111]

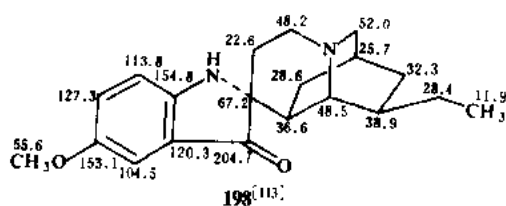


196[83]

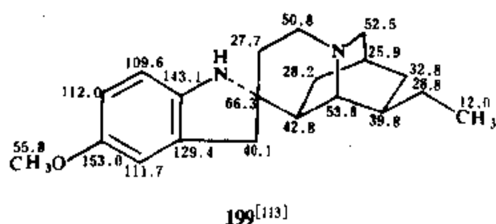


197[83]

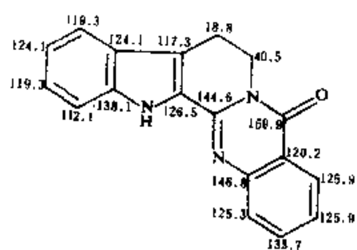
十四、其他单吲哚生物碱的^{13}C-NMR 化学位移



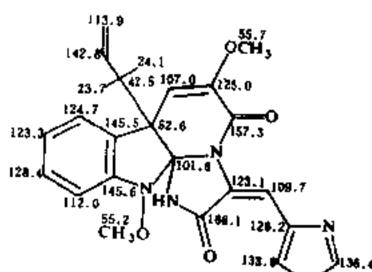
198[113]



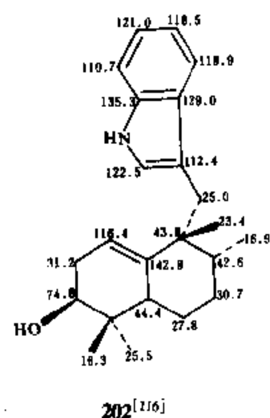
199[113]



200[114]



201[115]



202[116]

203[117]

204[118]

205[119]

206[120]

207[121]

208[122]

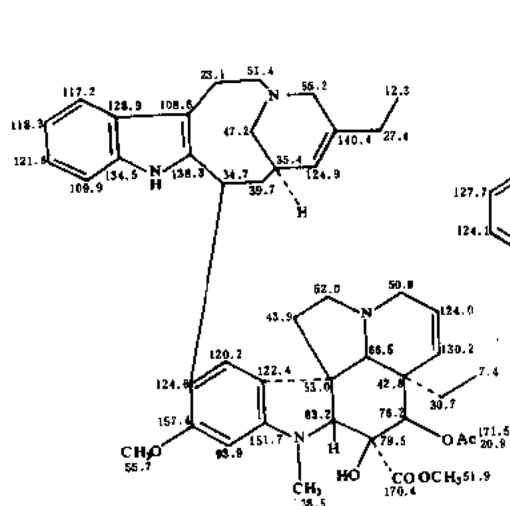
209[123]

210[117]

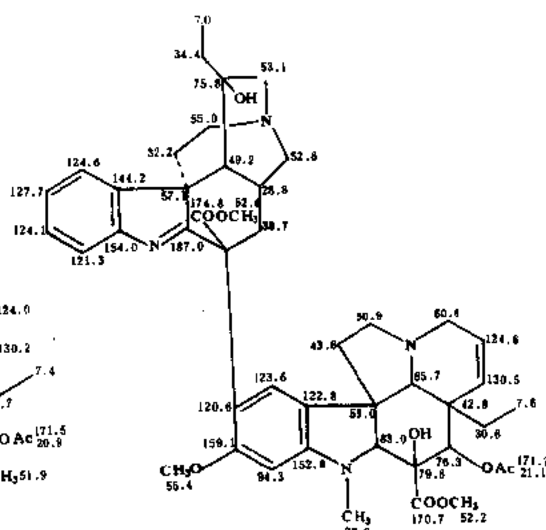
十五、双吲哚生物碱的^{13}C-NMR化学位移

211[88]

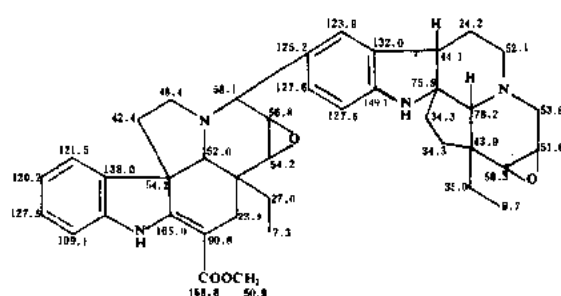
212[124]



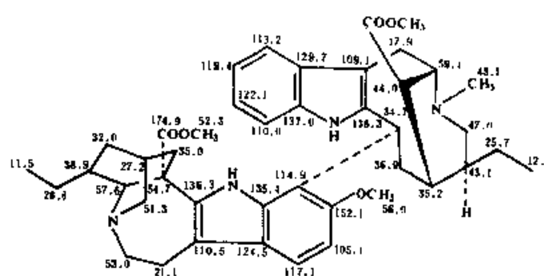
213[125]



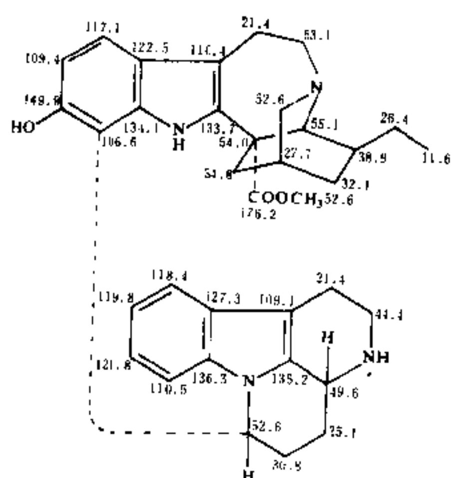
214[126]



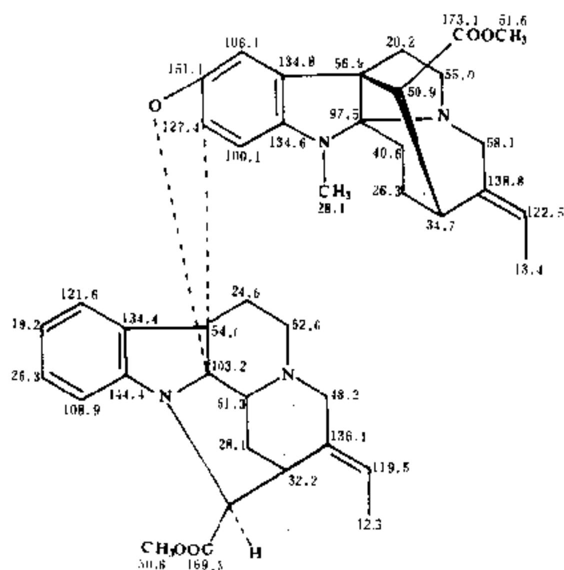
215[95]



216[88]



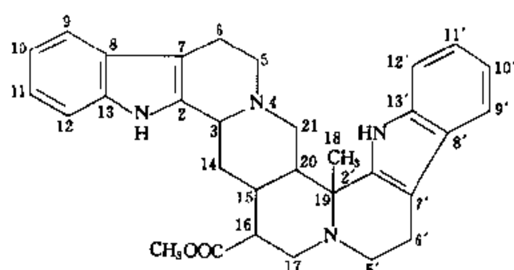
217[128]



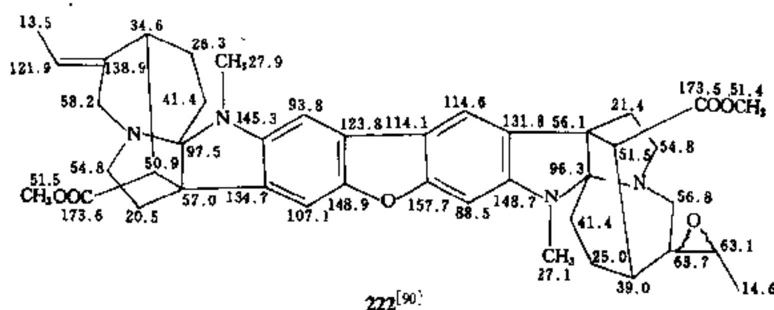
218[127]

表 20-27　双吲哚生物碱 219～221 的^{13}C-NMR 化学位移数据[129]

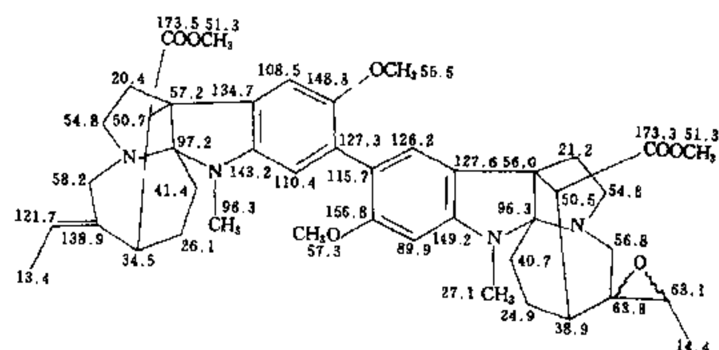
化合物 / C	219		220		221	化合物 / C	219		220		221
6	17.6	17.1	17.5	17.0	23.3	9,9′	116.4	118.1	118.7	118.0	118.1
CH_3(18)	18.1	18.7	26.9	26.6	18.7		117.0	118.7	118.8	118.0	118.8
6	23.0	22.6	23.0	22.3	22.7	10,10′	117.5	119.5	119.8	119.7	119.2
15	30.6	30.4	29.5	28.8	36.1		118.0	120.1	120.0	119.7	119.7
14	32.9	32.4	32.8	31.9	35.3	11,11′	119.5	121.5	122.1	121.9	121.1
21	48.1	47.8	48.6	46.7	57.9		120.4	122.5	122.4	122.2	122.2
20	49.4	50.6	49.3	48.4	50.0	8,8′	125.5	126.7	127.7	126.9	127.3
OCH_3	49.4	50.4	50.8	50.7	50.1		126.8	128.1	128.7	127.6	128.1
5	49.9	49.4	47.4	47.7	50.7	13,13′	135.3	136.2	137.7	136.5	137.4
5	51.4	51.2	52.1	51.3	54.0		135.3	136.2	137.4	136.1	137.3
3	54.0	54.2	55.1	54.2	60.6	2′	135.3	136.2	137.2	134.0	137.3
19	57.7	57.6	58.1	57.3	58.5	2	132.9	133.6	132.3	132.2	136.5
7	106.0	107.4	107.6	107.0	107.7	C=O	165.4	168.2	167.8	167.8	167.7
7	108.1	110.2	109.7	109.2	109.9	16	95.1	95.9	105.7	104.7	96.2
12,12′	110.2	111.4	112.2	111.6	111.7	17	144.8	146.9	149.1	148.3	146.9
	110.4	111.8	112.4	111.8	111.9						



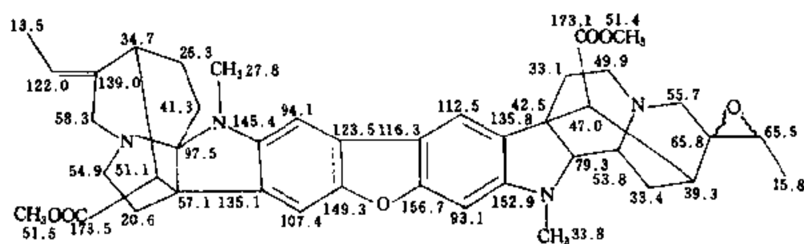
219. H(3β),H(15α),H(20β),C(18α)
220. H(3β),H(15α),H(20β),C(18β)
221. H(3α),H(15α),H(20β),C(18α)



222[90]



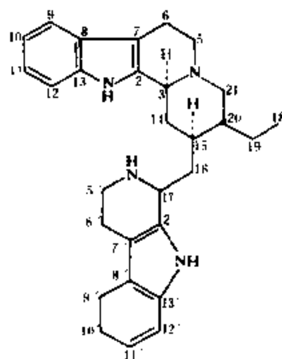
223[90]



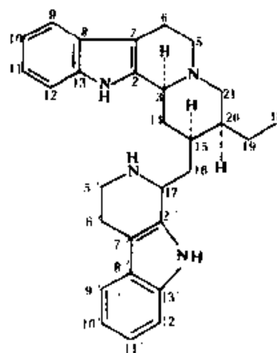
224[90]

表 20-28 双吲哚生物碱 225～228 的^{13}C-NMR 化学位移数据[130]

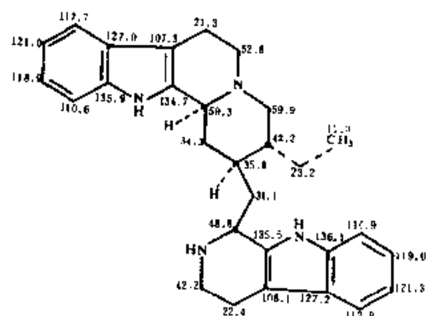
C \ 化合物	225	226	227	228
2,2′	124.7, 135.5	134.6, 135.5	135.2, 135.4	135.1, 135.4
3	59.3	59.5	59.4	60.3
5	52.6	52.9	53.1	53.1
6	21.5	21.6	21.5	21.6
7,7′	107.3, 108.1	107.3, 108.6	107.9, 108.7	107.3, 108.4
8,8′	127.0, 127.3	127.0, 127.2	127.3, 127.4	127.1, 127.2
9,9′	117.7, 117.9	117.7, 117.9	117.9, 118.0	117.7, 117.7
10,10′	121.0, 121.3	120.9, 121.6	120.9, 121.4	120.6, 121.2
11,11′	118.9, 119.0	118.9, 119.3	119.1, 119.2	118.8, 119.0
12,12′	110.6, 110.9	110.8, 110.8	110.6, 110.6	110.6, 110.6
13,13′	135.9, 136.1	135.8, 135.9	135.7, 136.0	135.8, 135.8
14	34.3	36.4	31.1	32.4
15	35.8	37.8	35.1	36.1
16	38.1	38.4	38.4	37.8
17	48.8	51.9	49.8	30.0
18	11.0	11.2	12.5	12.4
19	23.2	23.8	18.6	17.5
20	42.2	42.5	41.3	38.3
21	59.9	60.1	57.3	57.5
5′	42.2	42.0	42.3	42.2
6′	22.4	22.4	22.5	22.3



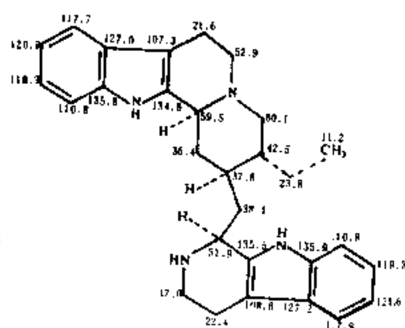
225. 17β-H
226. 17α-H



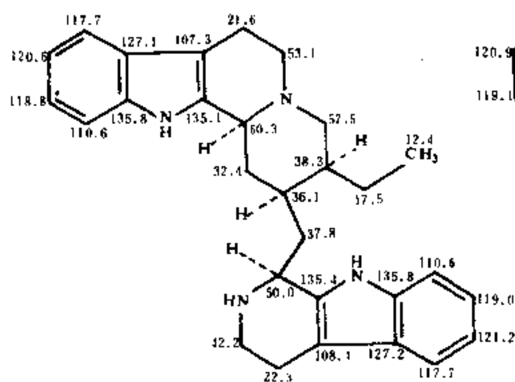
227. 17β-H
228. 17α-H



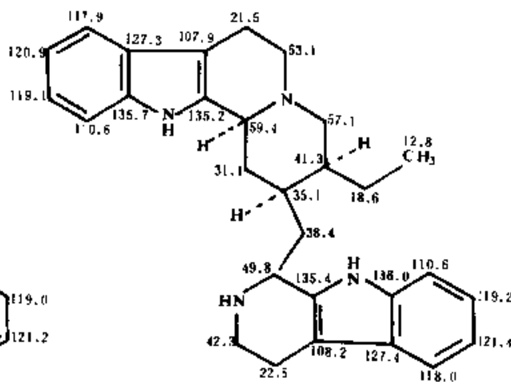
229[130]



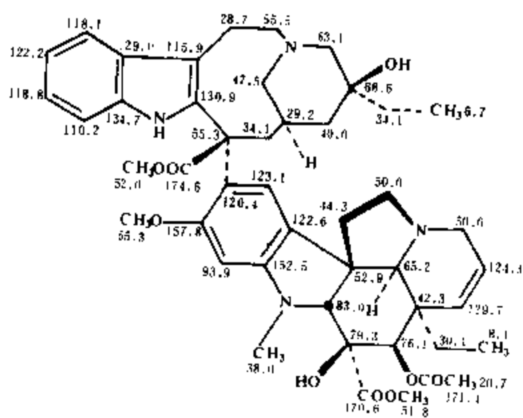
230[130]



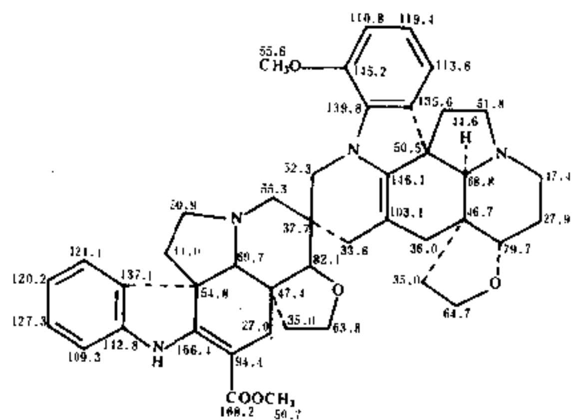
231[130]



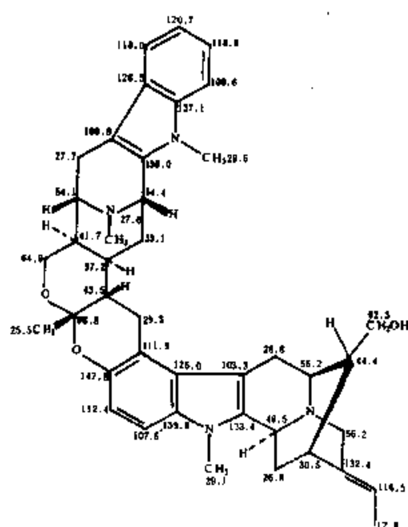
232[130]



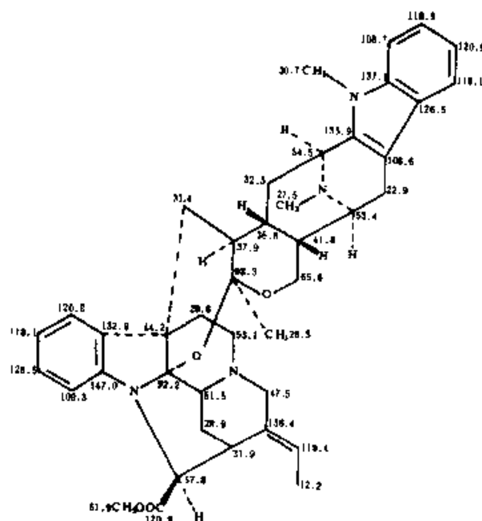
233[131]



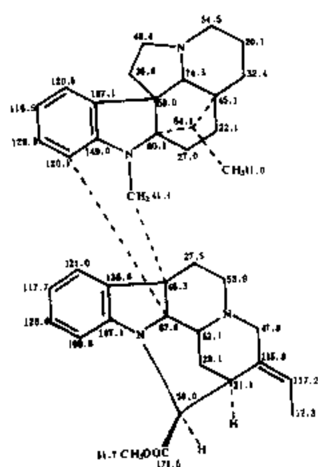
234[124]



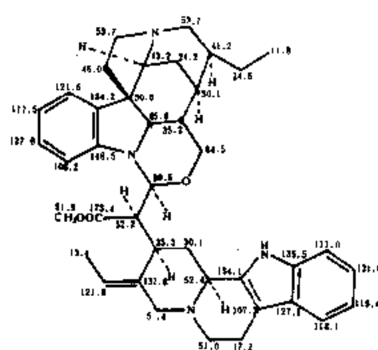
235[127]



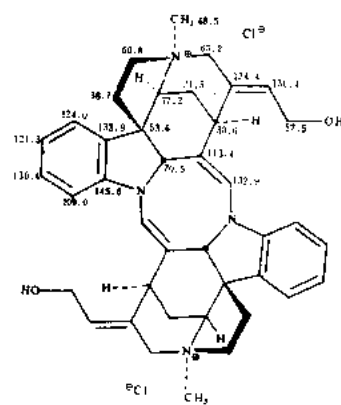
236[127]



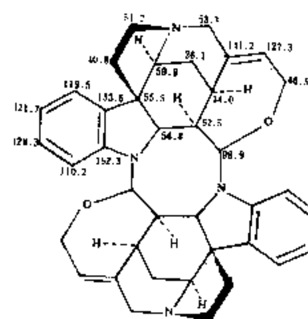
237[93]



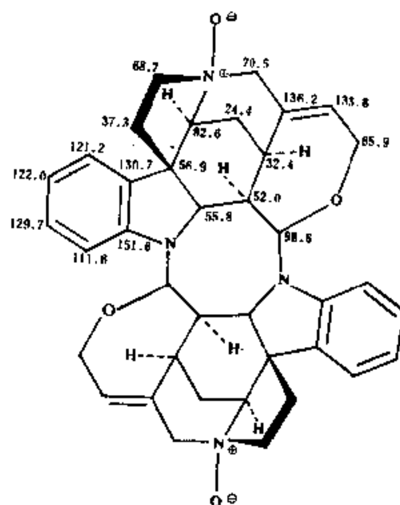
238[1H]



239[132]

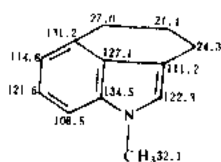


240[133]

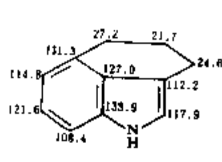


241[133]

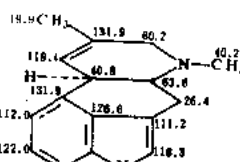
十六、麦角生物碱的^{13}C-NMR化学位移



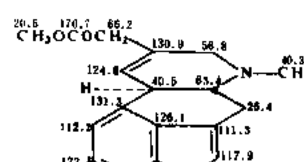
242[70]



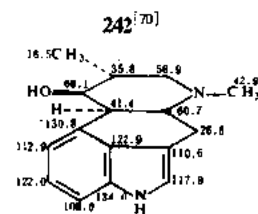
243[70]



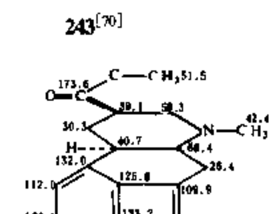
244[70]



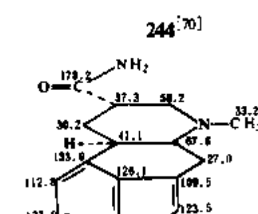
245[70]



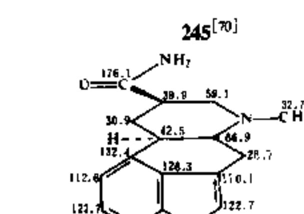
246[70]



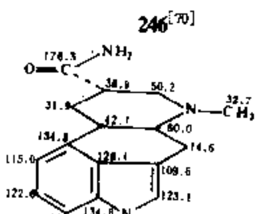
247[70]



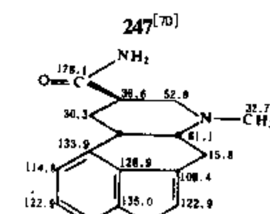
248[135]



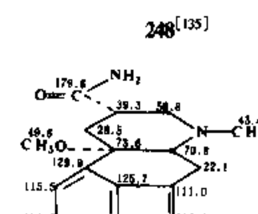
249[135]



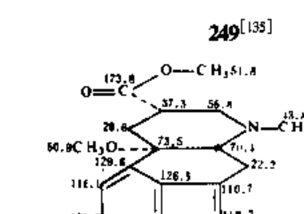
250[135]



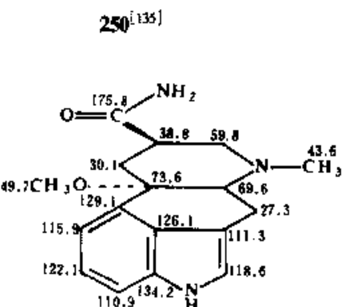
251[135]



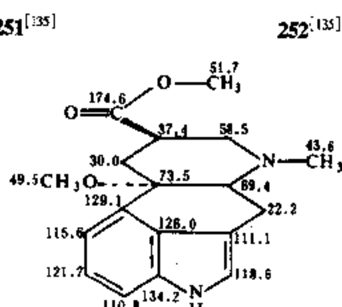
252[135]



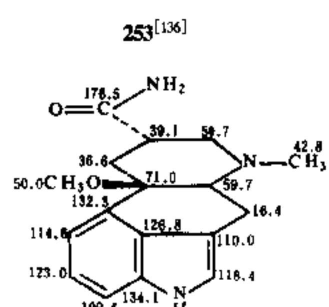
253[136]



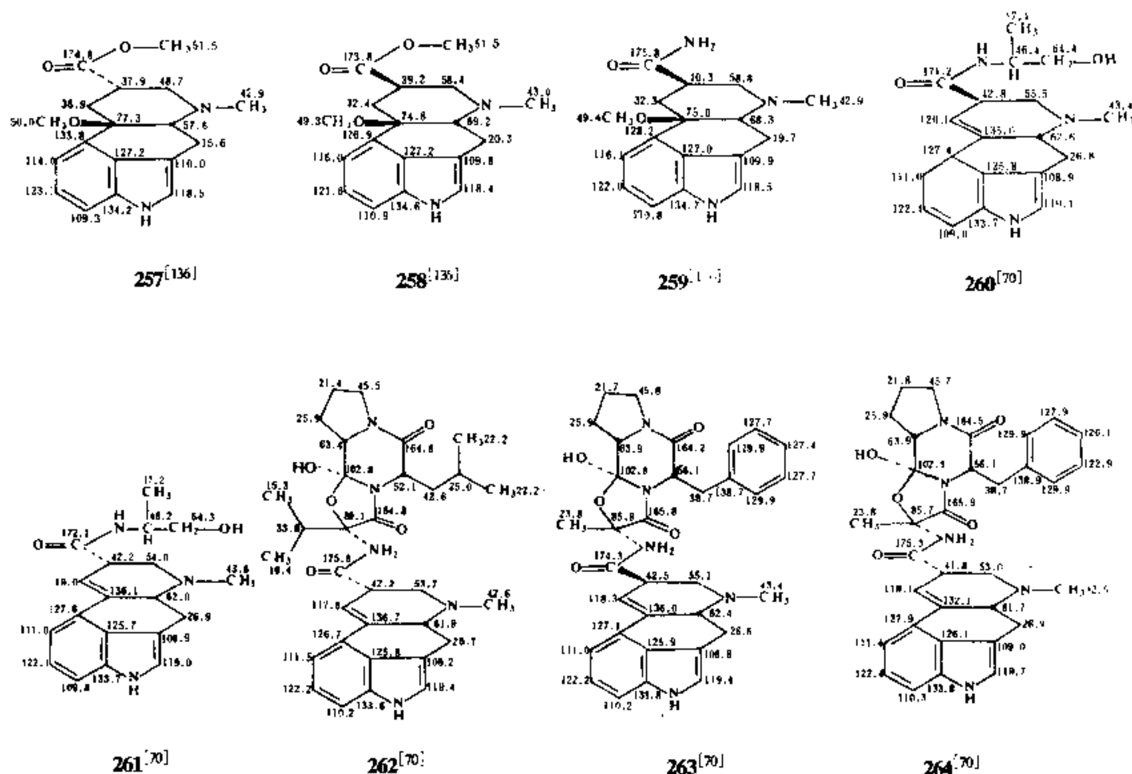
254[135]



255[136]



256[135]



257[136]　258[136]　259　260[70]

261[70]　262[70]　263[70]　264[70]

十七、其他吲哚类生物碱的^{13}C-NMR 化学位移

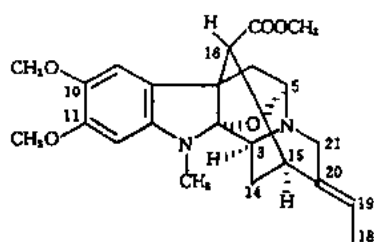
表 20-29　其他吲哚类生物碱 265～270 的^{13}C-NMR 谱化学位移数据[168]（一）

C \ 化合物	265	266	267①	268	269①	270①
2	109.1	109.3	109.8	189.5	167.6	167.5
3	49.7	49.4	48.9	51.5	60.2	59.8
5	87.2	87.2	86.7	90.0	53.3	53.1
6	40.6	44.4	43.6	38.6	56.1	55.9
7	50.0	52.6	52.1	53.9	56.1	55.9
8	126.2	135.2	134.7	137.4	127.2	127.0
9	110.5	114.6	114.8	107.3	120.0	119.9
10	144.3	154.4	154.0	149.3	105.5	105.7
11	149.7	111.9	111.0	147.1	159.8	159.9
12	95.0	109.3	108.9	104.8	96.9	97.1
13	143.1	145.0	144.5	149.2	144.6	145.0
14	25.7	22.0	21.4	36.1	28.2	26.4
15	31.2	36.2	35.7	32.6	30.3	24.8
16	52.1	56.8	56.4	56.5	98.1	98.3
17		67.6	67.3			
18	12.6	13.1	12.8	12.9	13.6	34.8
19	120.1	120.8	121.3	120.8	60.7	212.2
20	136.3	137.5	135.9	136.9	61.8	77.6
21	46.3	46.7	45.9	50.4	53.2	50.0
COOMe	172.6	172.2	172.0	171.7	170.8	171.4
	51.3	51.5	51.2	51.4	50.3	50.6

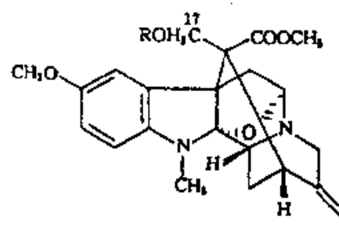
续表

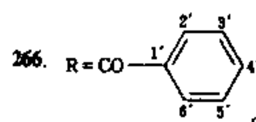
C \ 化合物	265	266	267①	268	269①	270①
OMe	57.1	55.2	54.7	56.5	54.9	55.2
	56.3			56.1		
				54.5		
N(1)-Me	29.8	30.3	29.7			
Acyl CO		165.3	165.0			
1′		129.6	121.4			
2′		129.5	111.8			
3′		128.6	148.1			
4′		132.6	152.7			
5′		128.6	109.9			
6′		129.5	123.3			
OMe			55.6			
			55.4			

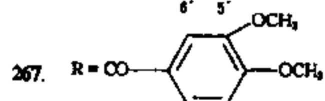
① 在 $CDCl_3 + CD_3OD$ 中测定。

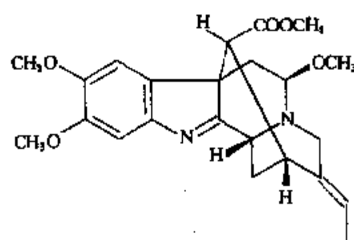


265.

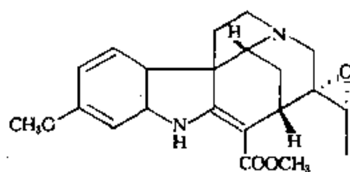




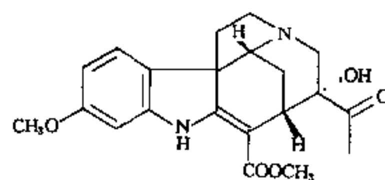




268



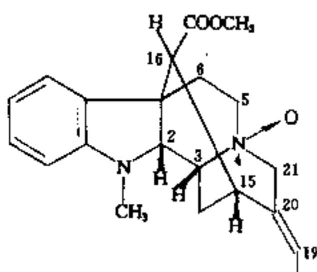
269



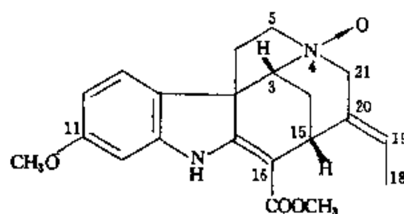
270

表 20-30 其他吲哚类生物碱 271～277 的 ^{13}C-NMR 谱化学位移数据[169]

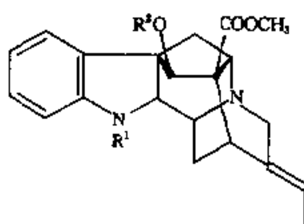
C \ 化合物	271	272	273	274	275	276	277
2	78.9	164.7	74.5	75.9	70.1	132.0	183.1
3	70.3	78.4	52.8	53.2	52.7	53.9	62.9
5	67.3	70.0	61.1	61.6	60.9	54.8	55.6
6	29.5	41.5	35.0	36.5	34.4	22.9	41.4
7	41.2	54.0	56.5	56.3	57.0	105.9	55.9
8	138.9	126.7	129.7	128.5	131.6	121.2	120.2
9	121.1	121.6	124.4	123.5	125.3	118.3	125.8
10	120.0	106.1	118.6	119.0	122.9	108.2	106.6
11	127.9	161.0	127.6	128.5	127.2	156.0	159.9
12	110.1	97.5	108.6	109.1	115.1	93.5	96.2
13	152.0	144.0	153.9	154.2	143.9	138.0	144.8
14	31.4	27.8	21.1	21.7	22.4	32.5	30.4
15	32.3	28.5	29.4	30.1	29.4	23.0	23.8
16	51.6	102.1	59.7	59.1	59.9	38.6	36.6
17			73.9	74.8	74.8	67.8	67.6
18	13.3	13.4	12.0	12.5	12.3	25.0	24.2
19	123.5	126.9	116.3	117.0	116.7	195.4	197.4
20	130.3	133.1	135.5	136.0	135.5	121.2	121.1
21	73.0	73.9	54.6	55.3	54.7	157.3	158.2
COOMe	171.9	167.1	173.0	172.2	173.0		
	51.7	51.3	50.8	51.6	51.2		
N(1)-Me	34.2		33.6	34.1		29.1	31.9
N(4)-Me						41.8	55.0
OMe		55.6		55.9	55.9	56.0	
					60.9		
ACyl-CO				163.8	169.7		
1′				122.1	130.5		
2′				112.0	105.9		
3′				148.6	153.2		
4′				152.9	141.2		
5′				110.4	153.2		
6′				123.2	105.9		



271



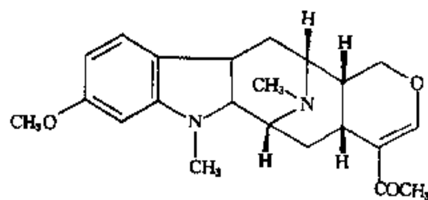
272



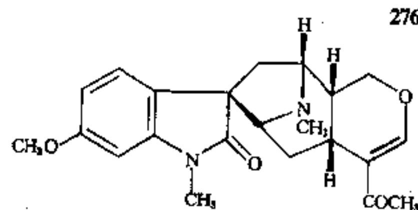
273. $R^1 = CH_3, R^2 = H$

274. $R^1 = CH_3, R^2 = CO$–(3,4-dimethoxyphenyl) (OCH_3, OCH_3)

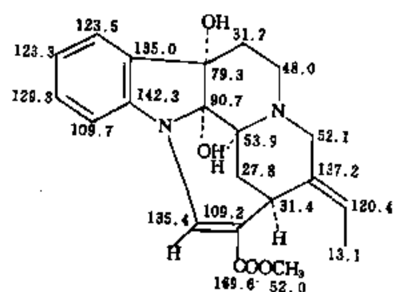
275. $R^1 = CO$–(3,4,5-trimethoxyphenyl) (OCH_3, OCH_3, OCH_3), $R^2 = H$



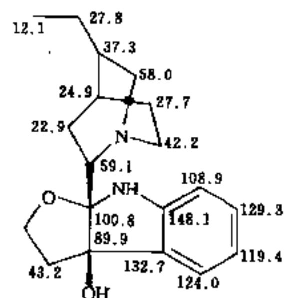
276



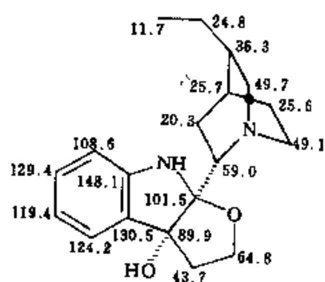
277



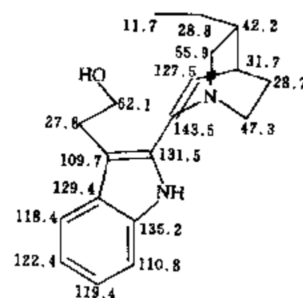
278[170]



279[171]



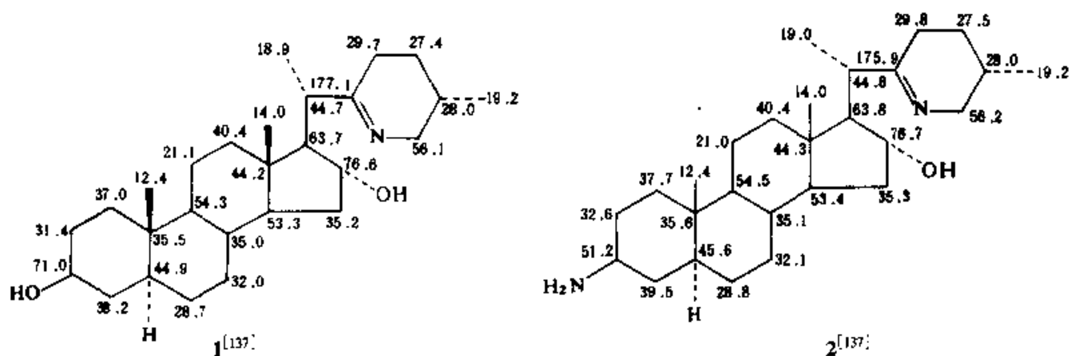
280[171]



281[171]

第九节　甾体和三萜类生物碱的^{13}C-NMR 化学位移

一、一般甾体生物碱的^{13}C-NMR 化学位移



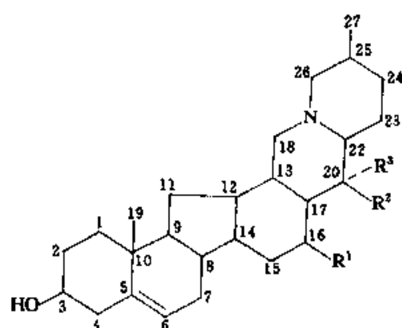
1[137]　　2[137]

二、异甾生物碱的^{13}C-NMR 化学位移

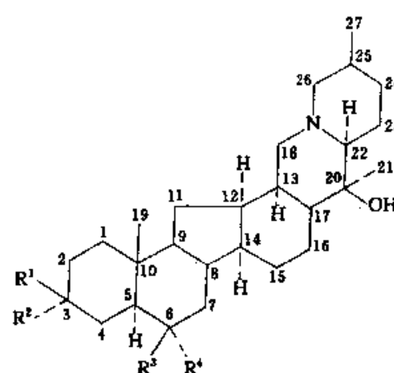
表 20-31　异甾生物碱 3～9 的^{13}C-NMR 化学位移数据[138]①

C \ 化合物	3	4	5	6	7	8	9
1	38.1	38.2	38.2	37.9	37.1	35.1	38.8
2	31.4(b)	31.5	31.5(b)	30.8	30.5(b)	28.7	31.2
3	72.0	71.9	71.9	71.4	70.9	66.9	71.9
4	41.8	41.9	42.0	32.5	30.1(b)	32.8	35.0
5	142.4	142.0	141.7	52.1	56.5(c)	42.6	48.3
6	122.3	122.3	122.6	70.3	211.0	72.6	72.6
7	31.2(b)	31.5	31.3(b)	40.5	46.0	39.1	39.1
8	38.6	38.7	38.7	39.1	42.1	35.6	35.8
9	54.4	54.3	54.6	56.8	56.7(c)	57.6	57.5
10	37.0	37.0	37.0	35.2	38.4	36.2	35.5
11	30.3(c)	29.5(b)	29.2(c)	29.4	29.4(d)	29.5(b)	29.6(b)
12	41.5	41.7	41.5	41.1	41.1	41.0	41.0
13	37.9	37.6	32.7	39.3	39.3	39.1	39.3
14	45.3(d)	44.7	43.7	44.0	43.5	43.8	43.8
15	25.1	25.2	30.8	24.8	24.7	24.8	24.9
16	24.9(e)	20.8	66.1	20.8	20.6	20.9	20.9
17	45.5(d)	49.0	50.4	49.0	48.8	49.0	49.0
18	62.6(f)	61.9(c)	61.6(d)	61.8(b)	61.8(c)	62.0(c)	61.9(c)
19	19.1	19.0	19.1	13.0	12.8	14.1	15.0
20	36.2	71.1	73.2	71.1	71.0	71.1	71.1
21	8.6	20.4	19.9	20.3	20.4	20.6	20.5
22	68.0	70.4	70.0	70.3	70.3	70.6	70.5
23	24.3(e)	19.2	18.7	19.1	19.1	19.1	19.1
24	28.9(c)	29.3(b)	28.8(c)	29.4	29.2(d)	29.3(b)	29.5(b)
25	28.3	27.8	27.6	27.7	27.7	27.8	27.8
26	63.9(f)	62.7(c)	62.2(d)	62.5(b)	62.3(c)	62.5(c)	62.6(c)
27	17.9	17.4	17.3	17.3	17.3	17.5	17.4

① (b)、(c)、(d)、(e)和(f)表示可以互换的数据。

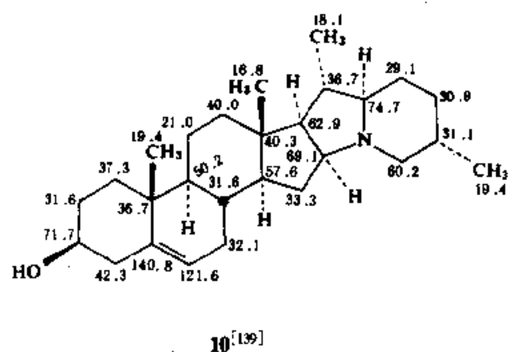


3. $R^1 = R^3 = H, R^2 = CH_3$
4. $R^1 = H, R^2 = OH, R^3 = CH_3$
5. $R^1 = R^2 = OH, R^3 = CH_3$

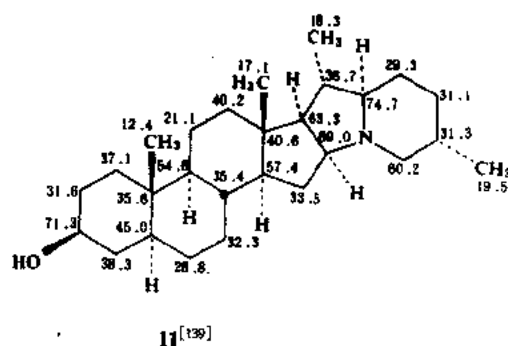


6. $R^1 = R^4 = OH, R^2 = R^3 = H$
7. $R^1 = OH, R^2 = H, R^3 + R^4 = O$
8. $R^1 = R^4 = H, R^2 = R^3 = OH$
9. $R^1 = R^3 = OH, R^2 = R^4 = H$

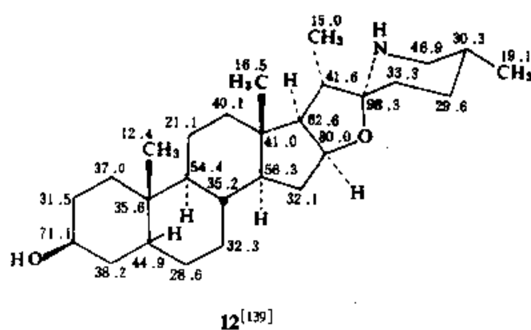
三、茄碱类化合物的^{13}C-NMR化学位移



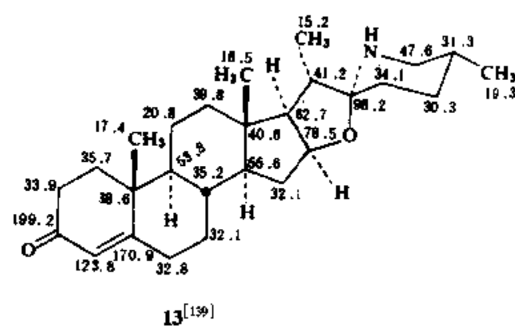
10[139]



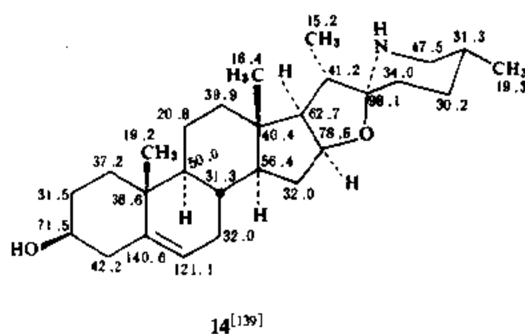
11[139]



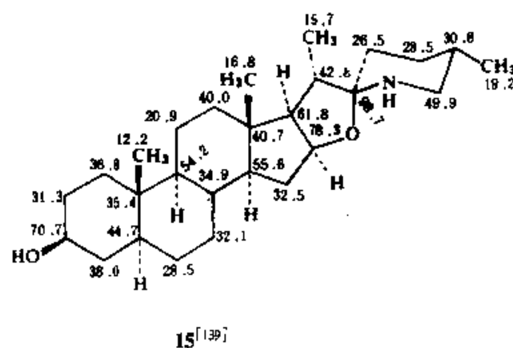
12[139]



13[139]



14[139]



15[139]

16[139]

17[139]

四、黄杨生物碱的^{13}C-NMR化学位移

18[140]

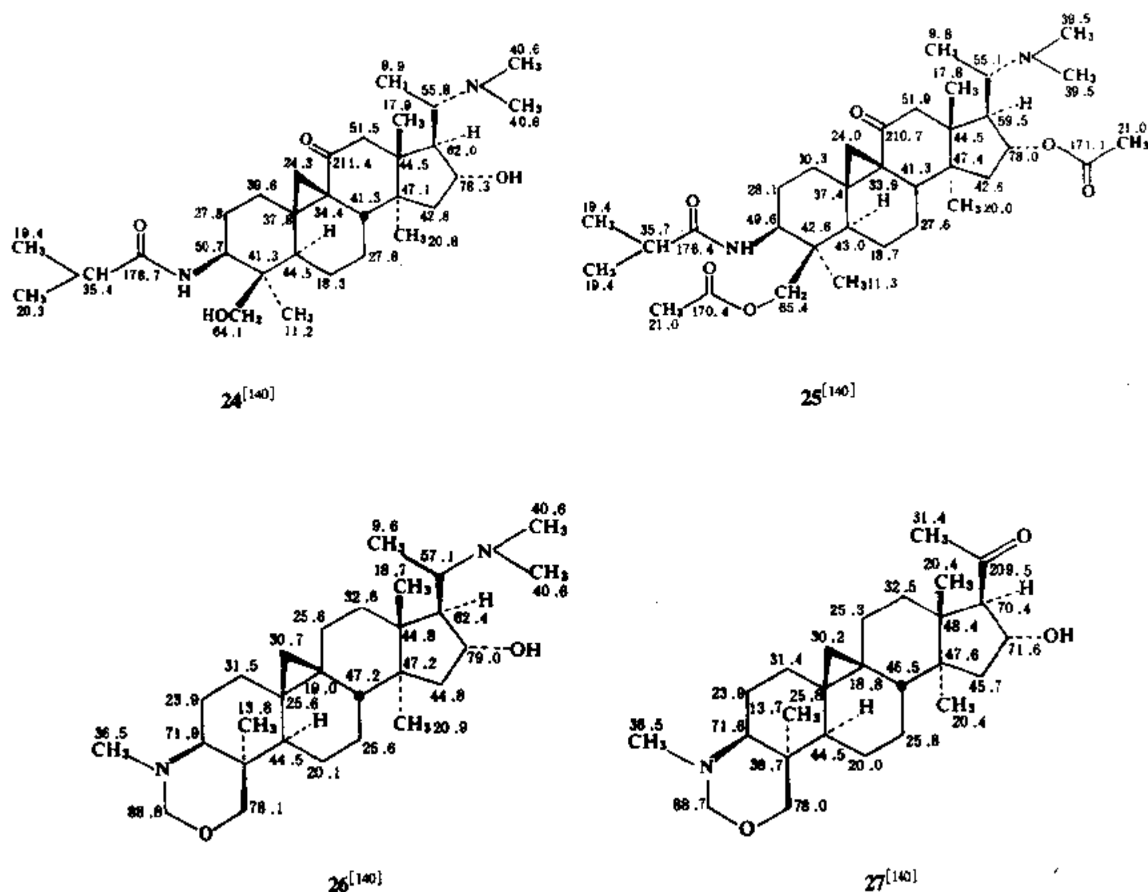
19[140]

20[140]

21[140]

22[140]

23[140]



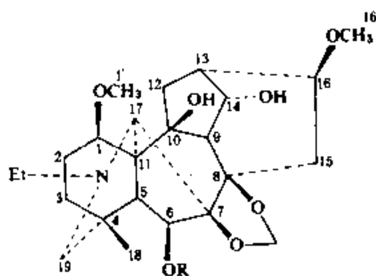
24[140]　25[140]　26[140]　27[140]

第十节　二萜类生物碱的^{13}C-NMR 化学位移

一、C_{19}类型二萜生物碱的^{13}C-NMR 化学位移

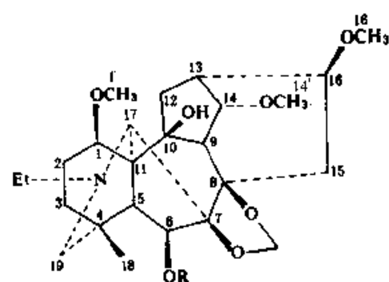
表 20-32　C_{19}类二萜生物碱 1～5 的^{13}C-NMR 化学位移数据[141]

C \ 化合物	1	2	3	4	5	C \ 化合物	1	2	3	4	5
1	78.7	79.9	79.2	80.2	83.1	15	32.9	33.2	34.8	34.3	33.3
2	26.4	26.4	27.1	27.0	26.4	16	81.2	81.2	81.5(b)	81.6	81.8
3	37.6	36.9	39.4	38.7	31.8	17	64.4	64.0	63.5	63.2	63.9
4	34.0	33.9	33.7	33.6	38.1	18	25.5	25.4	25.7	25.6	78.9
5	51.8	51.9	50.4	51.0	52.6	19	56.9	57.2	56.9	57.3	53.7
6	77.2	77.3	77.3	77.4	78.9	N—CH_2	50.4	50.5	50.2	50.4	50.7
7	93.0	93.4	91.6	92.4	92.7	CH_3	14.0	14.0	13.8	13.9	14.0
8	82.9	82.8	83.8	83.5	83.9	1′	55.6	55.6	55.3	55.5	55.5
9	50.4	51.6	50.4	51.5	48.1	O—CH_2—O	94.0	93.4	93.9	93.3	92.9
10	79.9	80.5	81.6	82.4	40.3	14′	—	—	57.7	57.9	57.8
11	55.1	55.4	56.0	56.2	50.2	16′	56.3	56.3	56.2	56.2	56.3
12	36.5	36.7	36.5	36.8	28.1	18′	—	—	—	—	59.6
13	36.6	36.5	38.5	37.6	37.9	6—OC=O	170.2	—	169.9	—	—
14	72.8	72.6	81.7(b)	81.6	82.5	CH_3	21.8	—	21.8	—	—



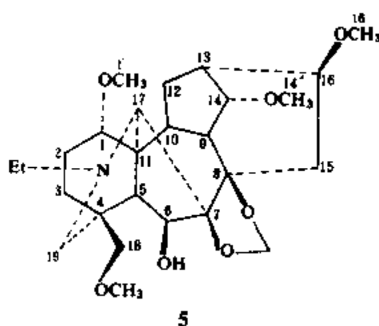
1. R = Ac

2. R = H

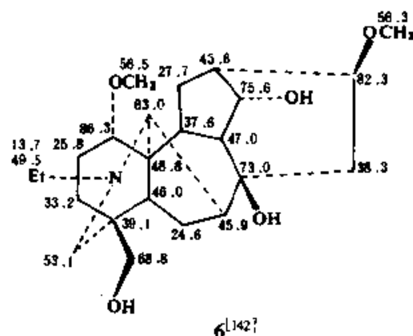


3. R = Ac

4. R = H



5

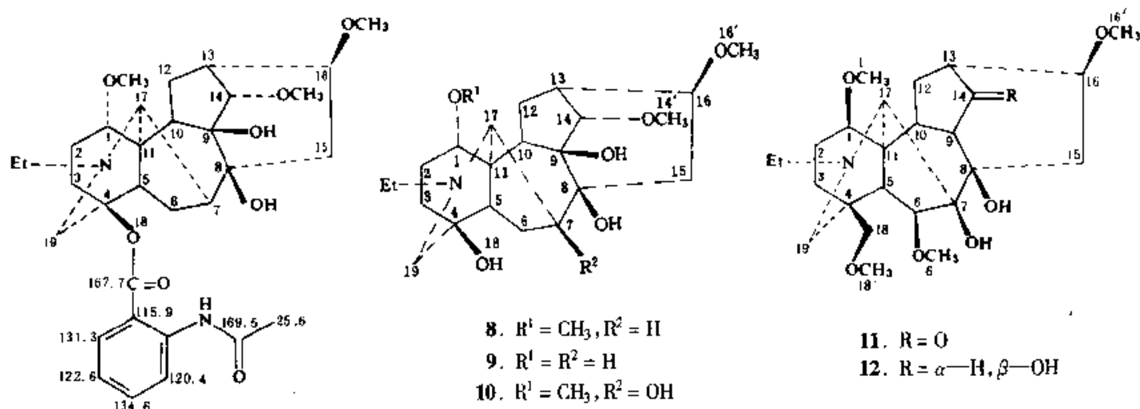


6[142]

表 20-33 C_{19}类二萜生物碱 7 ~ 12 的^{13}C-NMR 化学位移数据[143]

C \ 化合物	7	8	9	9①	10	11	12
1	84.2	85.2	72.5	73.0	84.9	85.5	85.2
2	26.2	26.6	29.8	30.7	27.1	25.5	25.5
3	31.9	36.3	33.5	34.6	36.8	32.5	32.5
4	84.7	71.1	70.7	70.0	71.1	38.5	38.4
5	48.6	50.8	48.2	48.3	51.1	46.1	45.1
6	26.8	26.9	27.4	27.9	32.4	89.8	90.1
7	47.6	47.8	47.0	47.6	78.0	88.9	89.1
8	75.6	75.7	76.3	75.5	86.5	85.5	76.3
9	78.6	78.8	77.6	78.2	78.7	53.8	49.6
10	36.4	37.4	36.3	37.1	37.5	43.9	36.4
11	51.0	51.0	50.4	51.0	51.4	49.0	48.2
12	24.2	23.7	23.1	24.0	26.3	29.7	27.5
13	49.0	49.0	48.4	47.9	51.1	49.5	46.1
14	90.2	90.3	90.4	90.8	90.2	216.3	75.3
15	44.9	44.7	45.1	44.2	38.1	33.1	33.1
16	82.9	83.1	83.0	83.9	83.0	85.5	81.7
17	61.5	61.7	63.1	62.9	63.2	65.9	65.4
18	—	—	—	—	—	77.9	78.0
19	55.5	58.0	60.4	61.5	56.8	52.7	52.7
N—CH_2	49.9	49.9	46.5	50.2	50.0	51.4	51.3
CH_3	13.5	13.5	13.1	13.2	14.5	14.3	14.3
1′	56.5	56.5	—	—	56.3	56.1	56.0
6′	—	—	—	—	—	57.6	57.5
14′	57.9	58.0	58.1	57.6	57.9	—	—
16′	56.1	56.1	56.3	56.0	56.3	56.3	56.5
18′	—	—	—	—	—	59.2	59.1

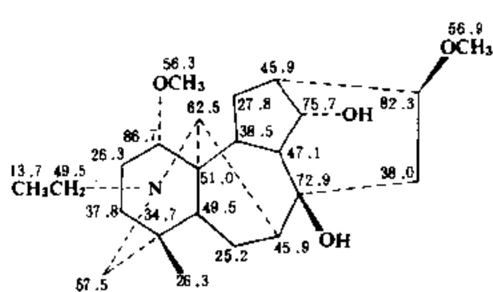
① 在 C_5D_5N 中测定。



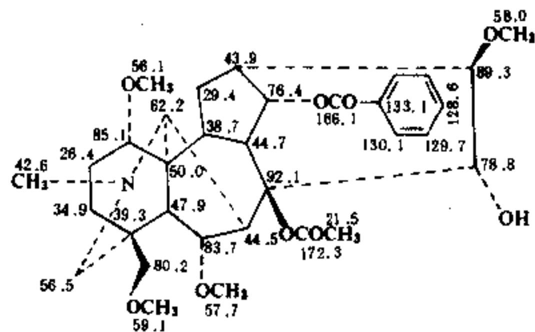
8. $R^1 = CH_3, R^2 = H$
9. $R^1 = R^2 = H$
10. $R^1 = CH_3, R^2 = OH$

11. R = O
12. R = α—H, β—OH

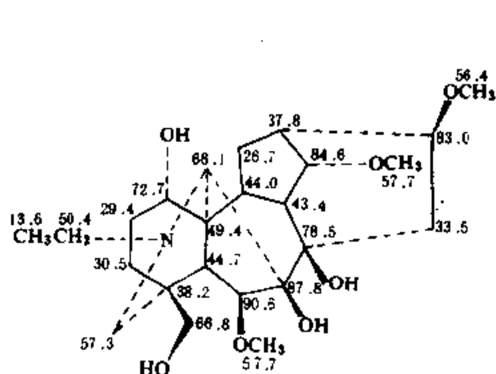
7



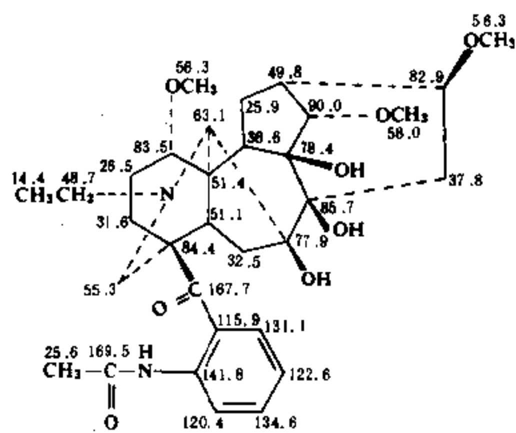
13[145]



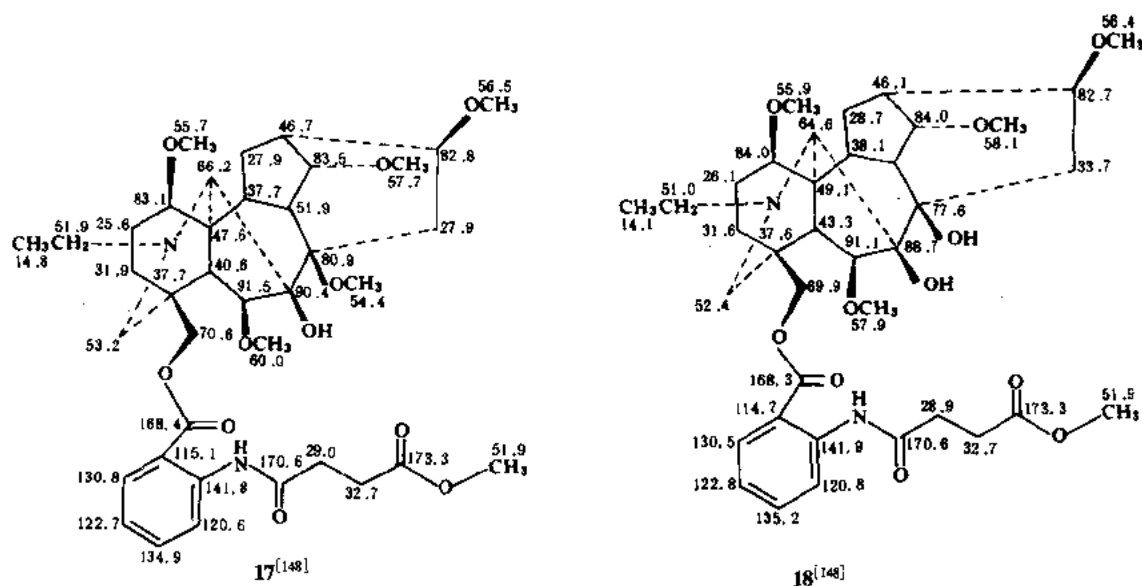
14[145]



15[146]



16[147]



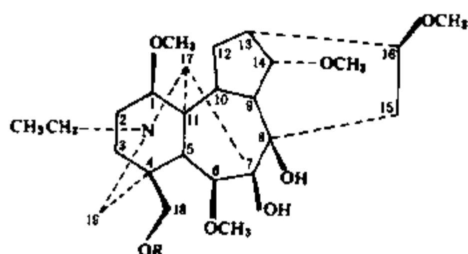
17[148]

18[148]

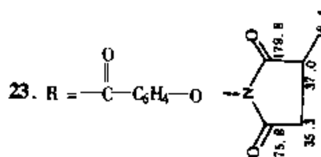
表 20-34 C_{19}类二萜生物碱 19～24 的^{13}C-NMR 化学位移数据[149]

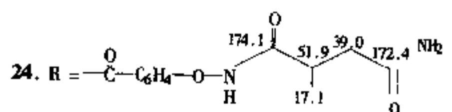
C \ 化合物	19	20	21	22	23	24
1	84.2(d)①	84.0	84.0	83.9	83.9	83.9
2	26.1	26.1	26.2	26.1	26.0	26.1
3	31.6	31.9	32.3	32.2	32.0	32.2
4	38.6	37.2	37.6	38.2	37.6	37.6
5	43.3	43.3	43.3	43.3	43.2	43.3
6	90.6	90.9	91.0	91.0	90.8	91.0
7	88.3	88.5	88.6	88.6	88.5	88.6
8	77.5	77.5	77.6	77.5	77.4	77.5
9	49.7	50.4	50.4	50.5	50.3	50.5
10	38.0	38.1	38.3	37.6	38.0	38.2
11	48.9	49.0	49.1	49.1	49.0	49.1
12	28.8	28.7	28.8	28.6	28.7	28.7
13	46.1	46.1	46.2	46.1	46.1	46.1
14	84.0(d)	84.0	84.0	83.9	83.9	83.9
15	33.7	33.7	33.7	33.8	33.6	33.8
16	82.7	82.6	82.6	82.6	82.5	82.6
17	64.8	64.6	64.6	64.5	64.5	64.5
18	67.6	69.1	68.7	69.8	69.5	69.8
19	52.9	52.4	52.6	52.5	52.3	52.4
N—CH_2	51.1	51.0	51.0	51.0	50.9	50.9
Me	14.1	14.1	14.1	14.0	14.0	14.0
1′	55.7	55.7	55.8	55.8	55.7	55.7
6′	57.7	57.8	57.9	57.8	57.8	57.8
14′	58.0	58.0	58.0	58.1	58.2	58.1
16′	56.2	56.3	56.3	56.3	56.3	56.3
—C=O	—	170.9	—	—	—	—
Me	—	20.8	—	—	—	—
—C=O	—	—	167.9	168.1	164.1	168.1
1	—	—	110.4	114.5	127.1	144.7,114.8
2	—	—	150.9	141.9	133.1	141.9,141.7
3	—	—	116.9(c)	120.6(c)	129.4	120.7(c)
4	—	—	134.4(d)	135.0(d)	133.6	134.9(d)
5	—	—	116.4(c)	122.5(c)	131.0	122.5(c)
6	—	—	130.8(d)	130.3(d)	130.0	130.3(d)

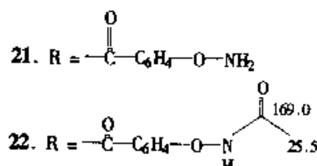
① (c)、(d)表示可以互换的数据。



19. R = H
20. R = Ac







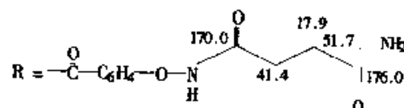
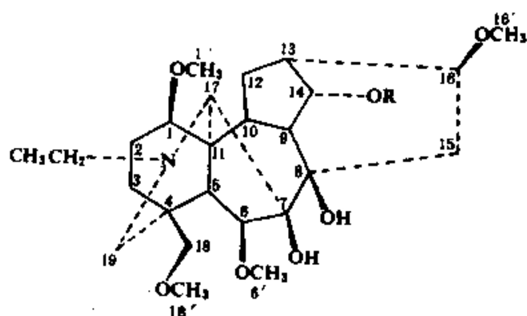


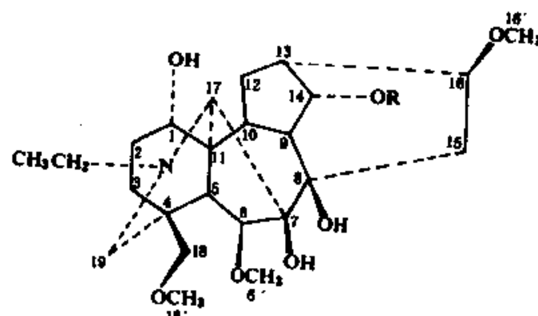
表 20-35　C_{19}类二萜生物碱 25～30 的^{13}C-NMR 化学位移数据[149]①

C \ 化合物	25	26	27	28	29	30
1	85.2	84.2	83.9(d)	72.7	72.6	72.6
2	25.5	26.2	26.2	27.5	27.2	27.2
3	32.5	32.4	32.4	29.4	29.9(d)	29.3
4	38.4	38.1	38.1	37.6	37.5	37.4
5	45.1	42.6	43.3	44.0	43.5(c)	43.9
6	90.1	90.3	90.6	90.1	90.2	90.4
7	89.1	88.3	88.4	87.9	87.6	87.8
8	76.3	77.1	77.5	78.1	78.4	78.5
9	49.6	51.2	49.8	45.3	44.9	44.9
10	36.4	38.1	38.1	39.4	38.0	37.7
11	48.2	49.5	48.9	48.9	49.2	49.3
12	27.5	28.2	28.7	29.4	29.4(d)	30.5
13	46.1	45.7	46.1	45.3	42.6(c)	43.3
14	75.3	76.0	84.3(d)	75.8	76.3	84.5
15	33.1	33.7	33.5	34.5	33.8	33.5
16	81.7	82.4	82.6	82.0	82.7	82.9
17	65.4	64.8	64.8	66.3	66.1	66.0
18	78.0	78.0	78.1	77.4	77.3	77.3
19	52.7	52.7	52.8	57.1	57.2	57.2
N—CH_2	51.3	48.8	51.1	50.4	50.3	50.3
CH_3	14.3	14.2	14.2	13.7	13.6	13.5
1′	56.0	55.8	55.7	—	—	—
6′	57.5	57.3	57.3	57.4	57.2	57.2
14′	—	—	57.8	—	—	57.9
16′	56.5	56.2	56.3	56.4	56.3	56.3
18′	59.1	59.0	59.0	59.1	59.1	59.1
—C=O	—	171.9	—	—	171.4	—
	—	21.5	—	—	21.4	—

① (c)和(d)表示可以互换的数据。



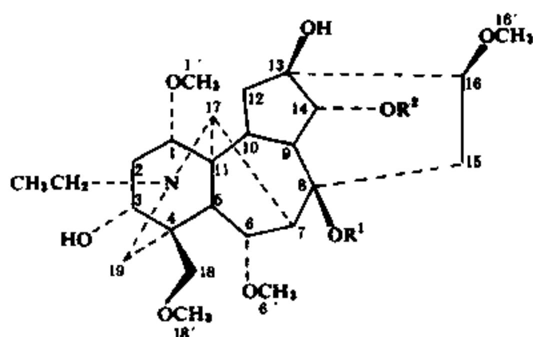
25. R = H
26. R = Ac
27. R = CH_3

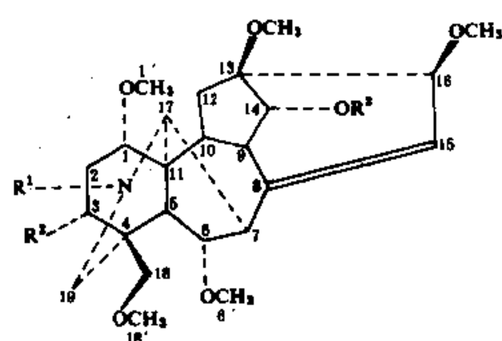


28. R = H
29. R = Ac
30. R = CH_3

表 20-36 C_{19}类二萜生物碱 31～36 的^{13}C-NMR 化学位移数据[149]

C \ 化合物	31	32	33	34	35	36	C \ 化合物	31	32	33	34	35	36
1	83.6	83.2	83.4	83.8	83.6	86.1	18	76.2	76.5	76.7	76.1	76.4	80.3
2	35.1	35.1	35.8	38.0	38.2	25.3	19	48.7	48.6	48.9	49.7	49.9	56.5
3	70.9	71.2	71.3	71.4	71.8	35.3	N—CH_2	47.2	47.2	47.5	47.7	47.9	42.7
4	43.1	43.0	43.3	44.0	44.1	40.0	CH_3	13.3	13.3	13.5	13.5	13.5	—
5	48.7	48.6	47.5	48.0	48.3	48.5	1′	55.7	55.6	55.8	56.2	56.3	56.5
6	82.1	82.0	82.5	83.7	83.6	83.6	6′	57.6	57.5	57.5	58.0	58.1	58.1
7	48.7	48.6	53.8	49.5	49.6	50.4	16′	58.7	58.5	58.3	57.3	57.2	57.2
8	85.3	85.3	73.6	146.6	146.5	146.6	18′	58.9	58.9	59.1	59.2	59.2	59.2
9	47.2	47.2	47.5	48.2	48.3	47.6	—CO	169.4	169.2	—	—	—	—
10	40.7	40.7	41.9	46.2	46.4	46.7	CH_3	21.5	21.5	—	—	—	—
11	50.1	50.0	50.2	51.6	51.7	51.9	—OC	165.6	165.7	166.2	167.5	168.0	168.0
12	33.7	33.5	33.7	33.4	33.4	38.4	(3,4-R-苯环)	122.5	129.7	122.5	122.9	130.2	130.5
13	74.7	74.5	75.8	77.4	77.6	77.7		110.2	129.2	110.5	110.3	130.0	130.0
14	78.4	78.5	79.8	78.1	78.3	79.1		152.8	128.1	153.1	153.0	128.2	128.1
15	39.6	39.4	42.4	116.1	116.4	116.3		148.4	132.7	148.6	148.5	132.8	132.7
16	83.0	82.8	82.5	83.1	83.1	83.6		111.8	—	112.3	112.5	—	—
17	61.4	61.4	61.6	77.8	78.5	78.6	R = OCH_3	55.7	—	55.8	55.9	—	—





31. R^1 = Ac, R^2 = 3,4-二甲氧基苯甲酰基

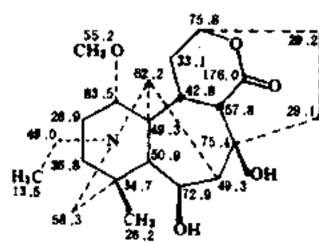
32. R^1 = Ac, R^2 = 苯甲酰基

33. R^1 = H, R^2 = 3,4-二甲氧基苯甲酰基

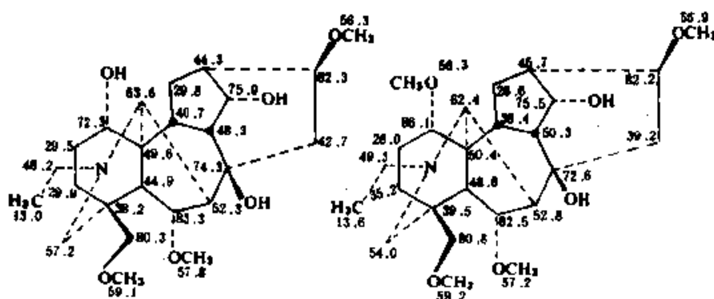
34. R^1 = Et, R^2 = OH, R^3 = 3,4-二甲氧基苯甲酰基

35. R^1 = Et, R^2 = OH, R^3 = 苯甲酰基

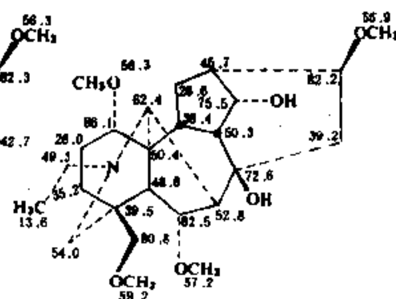
36. R^1 = CH_3, R^2 = H, R^3 = 苯甲酰基



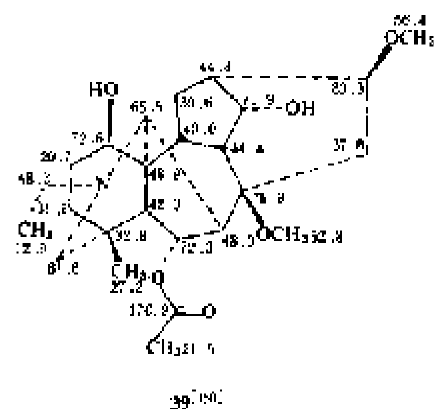
36[150]



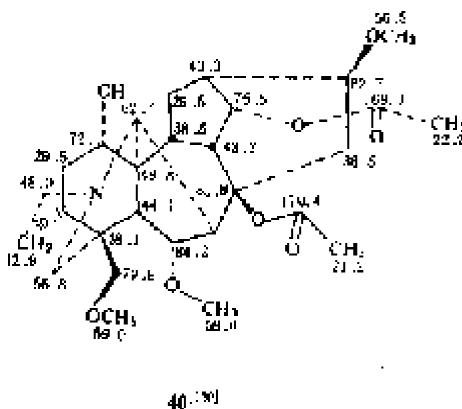
37[151]



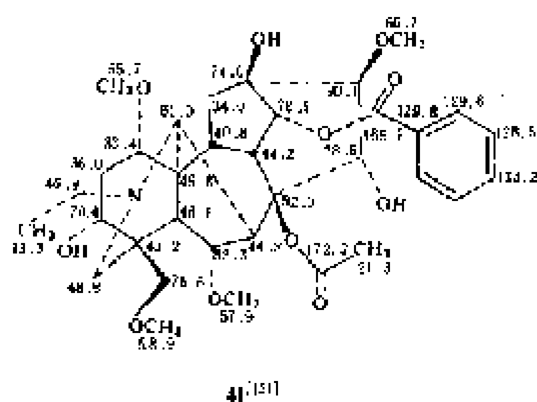
38[151]



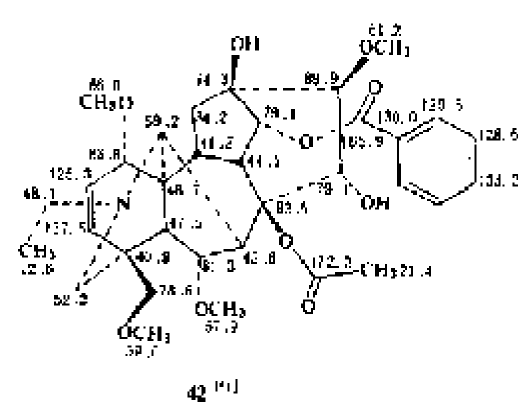
39[150]



40[150]



41[151]



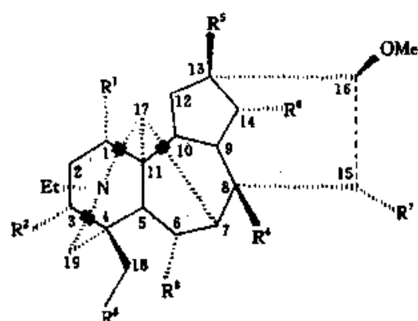
42[91]

表 20-37 C_{19}类二萜生物碱 43～52 的^{13}C-NMR 化学位移数据[172]

C \ 化合物	43	44	45	46	47	48	49	50	51	52
1	86.0	84.5	72.3	72.3	72.1	73.7	217.4	72.3	72.4	82.5
2	25.9	35.9	29.2	29.3	29.6	27.7	38.9	26.8	26.4	33.2
3	35.3	72.7	30.0	29.9	29.9	34.6	34.7	29.8	29.9	72.0
4	39.7	43.5	38.2	38.0	38.0	38.8	38.6	37.3	38.0	43.2
5	50.2	48.7	44.9	48.3	45.8	48.7	55.5	41.7	41.3	46.8
6	82.4	82.5	83.2	73.2	73.3	74.3	211.4	24.9	24.8	83.5
7	52.4	52.2	52.2	55.4	55.8	54.4	59.4	45.2	45.3	47.4
8	72.7	72.2	74.3	75.3	75.6	75.8	74.4	74.2	74.2	
9	50.6	50.4	48.4	45.9	46.3	46.9	44.5	46.8	46.8	48.9
10	42.4	42.0	44.2	44.3	43.6	44.5	39.9	44.3	44.2	41.8
11	50.2	50.2	49.5	50.0	50.2	49.6	57.2	49.2	48.7	50.2
12	36.0	35.8	29.4	29.5	29.6	29.3	31.5	28.3	28.3	37.0
13	76.8	75.8	40.3	40.4	37.0	37.3	37.7	39.9	39.9	79.0
14	79.8	79.6	76.1	76.2	77.1	77.1	75.5	76.0	76.0	79.0
15	39.5	39.9	42.9	42.7	42.3	39.8	41.5	42.4	42.4	61.9
16	84.7	83.1	82.8	81.8	82.0	82.5	82.2	81.9	81.9	90.6
17	62.7	62.2	63.8	63.9	63.4	61.9	63.1	64.1	64.1	61.2
18	80.8	77.4	80.3	80.6	80.5	80.3	76.2	79.1	68.4	77.5
19	53.8	47.4	57.1	57.2	57.1	55.1	54.9	56.5	56.5	49.0
20	49.4	49.2	48.4	48.6	48.3	49.6	48.9	48.6	48.6	47.6
21	13.8	13.7	13.1	13.1	13.1	13.5	13.1	13.1	13.1	13.3

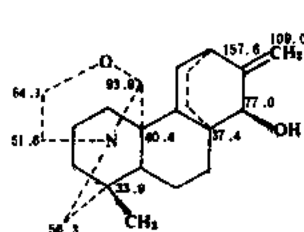
续表

C \ 化合物	43	44	45	46	47	48	49	50	51	52
1′	56.3	56.2								55.8
6′	57.4	57.8	57.2							58.0
16′	57.7	57.3	56.3	56.4	56.2	56.2	56.3	56.3	56.5	61.3
18′	59.3	59.3	59.2	59.3	59.3	59.3	59.3	59.4		59.2
C=O					170.6	170.1	171.1			
						170.2				
						170.2				
					21.3	21.4	21.3			
						21.7				
						22.0				

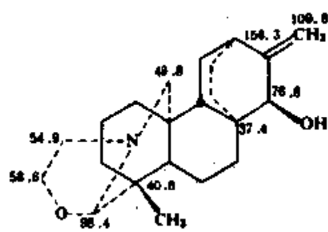


43. $R^1 = R^3 = R^8 = OMe, R^2 = R^7 = H, R^4 = R^5 = R^6 = OH$
44. $R^1 = R^3 = R^8 = OMe, R^2 = R^4 = R^5 = R^6 = OH, R^7 = H$
45. $R^1 = R^4 = R^6 = OH, R^2 = R^5 = R^7 = H, R^3 = R^8 = OMe$
46. $R^1 = R^3 = R^4 = R^6 = OH, R^2 = R^5 = R^7 = H, R^8 = OMe$
47. $R^1 = R^3 = R^4 = OH, R^2 = R^5 = R^7 = H, R^6 = OAc, R^8 = OMe$
48. $R^1 = R^3 = R^6 = OAc, R^2 = R^5 = R^7 = H, R^4 = OH, R^8 = OMe$
49. $R^1 = R^3 = O, R^2 = R^5 = R^7 = H, R^4 = OH, R^6 = OAc, R^8 = OMe$
50. $R^1 = R^4 = R^6 = OH, R^2 = R^3 = R^5 = R^7 = H, R^8 = OMe$
51. $R^1 = R^4 = R^6 = R^8 = OH, R^2 = R^3 = R^5 = R^7 = H$
52. $R^1 = R^3 = R^8 = OMe, R^2 = R^4 = R^5 = R^6 = R^7 = OH$

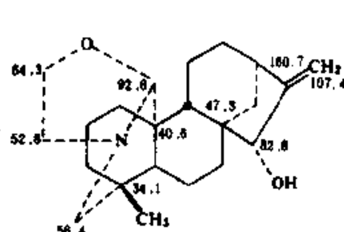
二、C_{20}类型二萜生物碱的^{13}C-NMR化学位移



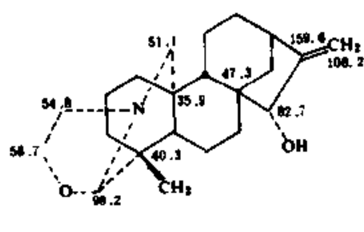
53[152]



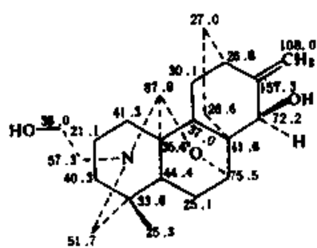
54[152]



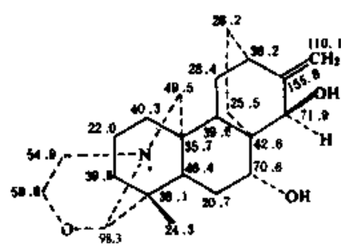
55[152]



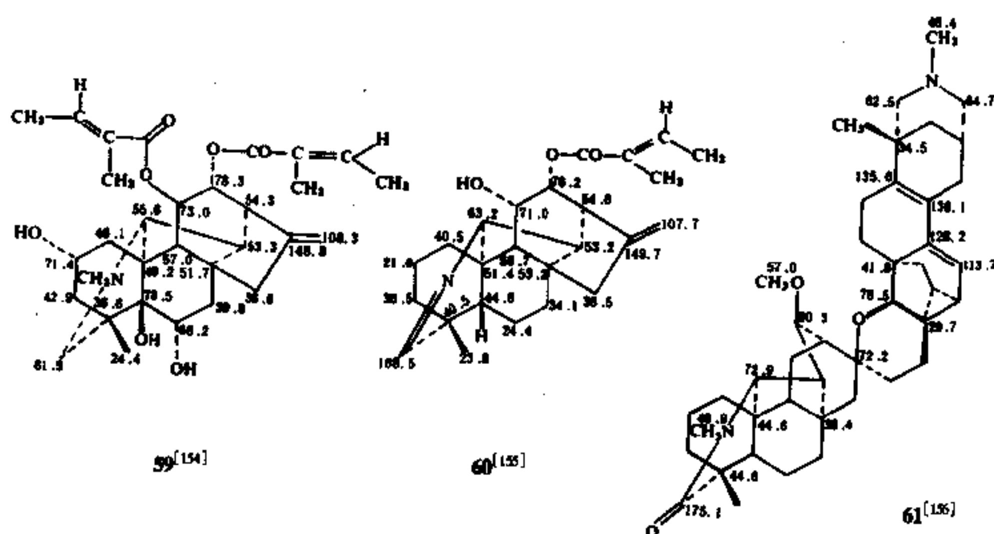
56[152]



57[153]



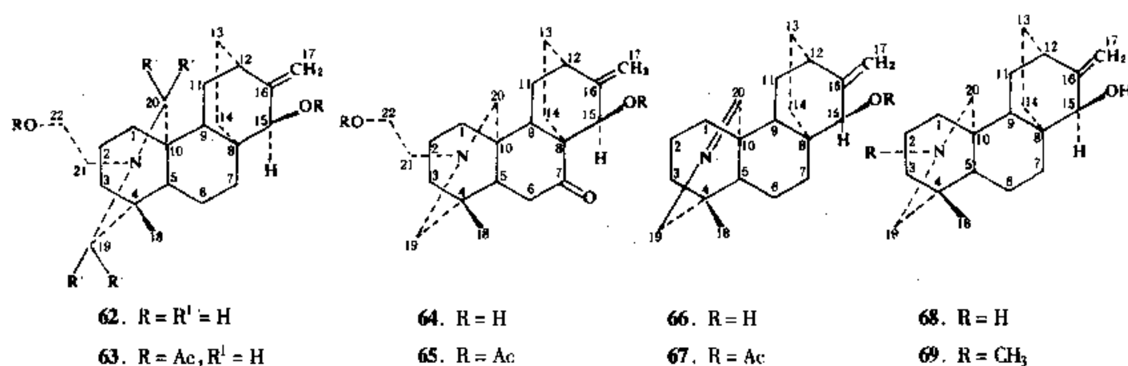
58[153]



59[154]　　60[155]　　61[156]

表 20-38　C_{20}类二萜生物碱 62～69 的 ^{13}C-NMR 化学位移数据[157]

C \ 化合物	62	63	64	65	66	67	68	69
1	40.2	40.5	40.7	41.0	42.4	42.4	40.6	41.9
2	23.2	23.2	22.6	23.3	20.0	20.0	23.3	22.5
3	41.4	41.8	39.1	39.3	34.1	34.1	31.5	40.7
4	33.6	33.6	33.5	33.5	32.8	32.9	32.4	33.7
5	49.6	49.9	47.9	47.4	46.9	47.0	49.7	45.5
6	17.4	17.3	36.2	36.2	19.6	19.4	17.6	17.4
7	31.5	31.9	215.8	211.5	31.0	31.2	31.6	31.7
8	37.4	36.8	53.0	50.8	37.4	36.7	37.5	37.6
9	39.5	40.5	41.6	42.3	38.1	39.2	39.7	39.6
10	38.0	38.2	37.2	37.3	42.5	42.5	36.5	38.2
11	28.0	28.0	28.0	27.8	28.1	28.0	28.0	28.2
12	36.4	36.4	36.0	36.1	36.0	35.9	35.5	36.5
13	27.7	27.4	26.6	26.8	26.1	25.8	27.7	27.7
14	26.4	26.3	25.3	25.6	25.5	25.0	26.4	26.5
15	76.8	77.2	72.8	73.6	75.2	76.2	76.7	77.0
16	156.3	151.3	151.5	149.2	156.2	151.1	156.4	156.8
17	109.6	110.7	109.5	110.8	108.9	110.1	109.5	109.5
18	26.4	26.3	25.8	25.6	25.8	25.8	26.4	26.4
19	60.2	60.4	58.9	59.1	60.2	60.7	51.8	62.7
20	54.0	53.9	53.5	52.9	166.4	165.1	45.6	56.2
21	58.0	57.2	58.0	57.0	—	—	—	46.9
22	60.7	61.6	60.5	61.1	—	—	—	—
—C=O	—	170.9	—	170.3	—	170.8	—	—
	—	170.6	—	169.9	—	—	—	—
CH_3	—	21.3	—	21.9	—	21.2	—	—
	—	20.9	—	21.0	—	—	—	—

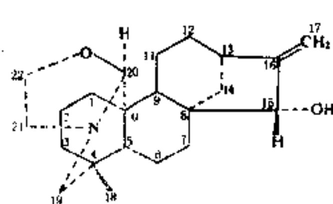


62. R = R¹ = H　　64. R = H　　66. R = H　　68. R = H

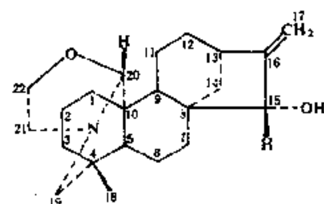
63. R = Ac, R¹ = H　　65. R = Ac　　67. R = Ac　　69. R = CH_3

表 20-39　C_{20}类二萜生物碱 70～78 的^{13}C-NMR 化学位移数据[157]

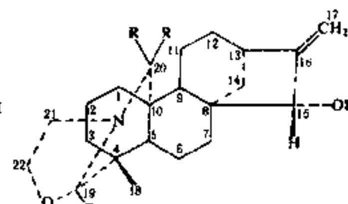
C \ 化合物	70	71	72	73	74	75	76	77	78
1	41.7	41.3	40.6	41.2	41.6	42.3	42.4	40.8	41.7
2	18.6	19.2	20.6	18.5	18.3	18.3	18.4	18.3	18.2
3	37.1	37.1	40.6	40.7	40.9	34.9	35.4	40.3	41.2
4	34.1	34.1	40.3	33.6	33.6	32.9	32.9	32.7	33.8
5	52.8	52.3	50.6	50.4	49.9	49.7	49.0	51.0	50.6
6	18.6	17.4	18.2	18.2	18.3	18.3	18.4	18.3	18.2
7	33.9	33.9	33.8	33.2	32.7	32.9	31.8	33.6	33.4
8	47.3	47.5	47.4	47.2	47.0	47.3	47.0	47.5	47.4
9	51.6	51.1	49.1	50.0	49.9	49.7	49.0	50.7	50.0
10	40.6	40.3	35.9	40.2	40.2	45.5	45.5	39.2	40.3
11	22.7	21.8	22.3	23.4	22.4	20.9	20.6	23.7	22.7
12	31.2	30.3	32.4	32.3	32.4	32.9	33.1	32.3	32.4
13	42.4	42.4	41.7	41.7	41.9	42.3	42.2	41.9	41.9
14	35.1	35.1	36.8	36.8	37.6	34.6	34.9	36.5	36.7
15	82.8	84.3	82.7	82.3	82.7	80.6	81.3	82.7	82.8
16	160.7	161.2	159.6	159.1	154.8	159.7	154.8	160.0	159.9
17	107.4	107.8	108.5	108.2	109.9	107.9	109.8	108.3	108.3
18	25.9	26.4	24.4	26.4	26.3	26.0	26.0	26.6	26.5
19	56.4	55.9	98.2	60.2	60.3	58.9	59.5	52.8	62.7
20	92.6	93.3	51.1	55.9	55.8	165.8	165.9	48.0	58.2
21	50.2	49.8	54.8	57.8	57.2	—	—	—	47.0
22	64.3	58.8	58.7	60.6	61.4	—	—	—	—
—C=O	—	—	—	—	170.2	—	170.1	—	—
CH₃	—	—	—	—	170.2	—	—	—	—
	—	—	—	—	21.0	—	21.0	—	—
	—	—	—	—	21.0	—	—	—	—



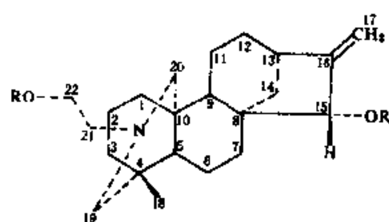
70



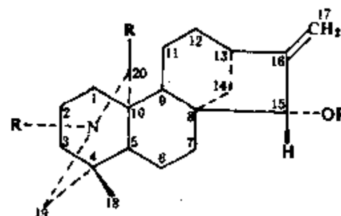
71



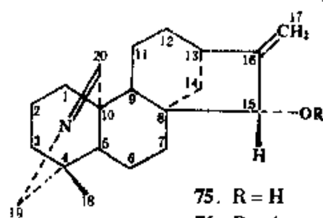
72. R = H



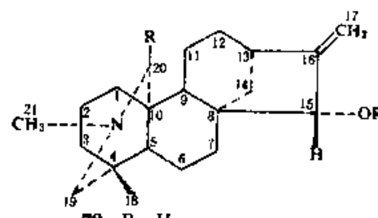
73. R = H
74. R = Ac



77. R = H



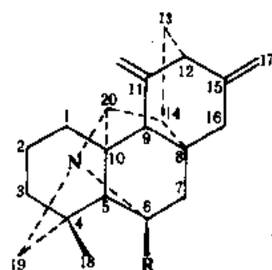
75. R = H
76. R = Ac



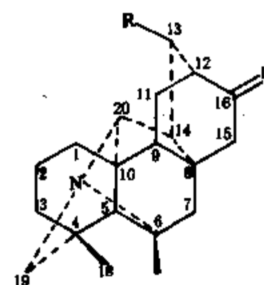
78. R = H

表 20-40　C_{20}类二萜生物碱 79～82 的^{13}C-NMR 化学位移数据

C \ 化合物	79	80	81	82	C \ 化合物	79	80	81	82
1	35.6	34.9	35.2	34.6	11	211.0	22.7	211.2	21.8
2	19.2	19.3	19.3	19.1	12	53.3	53.3	53.4	49.8
3	33.8	33.7	33.9	33.6	13	27.6	213.0	28.3	67.7
4	37.7	38.0	38.0	37.1	14	43.9	60.9	45.0	41.9
5	61.9	61.2	61.0	58.1	15	29.2	26.0	28.4	24.0
6	98.7	65.4	65.6	65.7	16	143.5	142.7	144.1	147.2
7	45.2	33.9	35.2	33.3	17	110.9	110.4	110.1	107.0
8	44.5	43.0	44.2	42.2	18	30.6	28.8	28.8	28.5
9	65.2	48.9	65.3	49.1	19	60.8	62.7	63.1	59.8
10	51.8	49.8	51.0	50.1	20	74.6	70.0	75.7	69.1



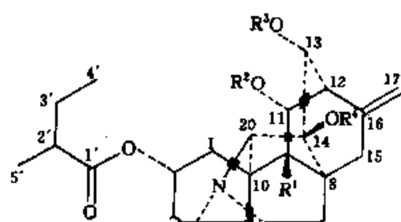
79. R = OH
81. R = H

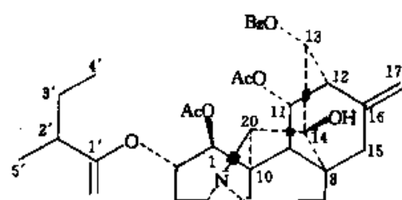


80. R = O
82. R = OH

表 20-41 C_{20}类二萜生物碱 83～88 的^{13}C-NMR 谱化学位移数据[173]

C \ 化合物	83	84	85	86	87	88
1	29.9	29.7	31.1	28.8	29.7	72.4
2	67.9	68.0	67.2	68.1	67.9	65.8
3	73.9	74.1	73.1	74.2	73.5	70.9
4	42.2	42.2	41.1	41.8	41.2	42.5
5	61.1	61.6	60.4	55.7	55.0	58.0
6	62.5	62.6	63.2	61.8	62.6	62.5
7	31.3	31.6	31.3	26.4	26.1	31.3
8	44.9	44.7	44.0	50.6	50.7	44.9
9	51.3	53.2	53.3	80.9	81.0	49.7
10	45.6	45.9	46.1	47.3	46.7	49.5
11	75.1	74.7	75.6	84.0	85.3	74.9
12	46.1	49.7	51.6	48.4	51.0	47.9
13	80.5	81.1	80.8	80.4	79.7	80.4
14	78.6	78.8	80.2	77.3	78.5	78.6
15	30.6	30.7	30.5	27.9	28.0	30.7
16	141.8	143.3	143.0	143.1	143.6	141.5
17	110.6	109.5	108.7	109.5	108.8	110.6
18	25.4	25.4	22.5	25.7	25.8	25.3
19	59.6	59.6	58.6	59.9	59.4	59.1
20	69.3	69.5	69.2	68.0	67.7	67.0
1′	175.7	175.7	175.6	175.9	175.9	174.5
2′	41.4	41.4	41.5	41.3	41.6	39.6
3′	26.2	26.1	26.6	26.1	26.6	24.9
4′	11.6	11.6	11.5	11.5	11.6	10.7
5′	17.1	17.2	17.0	17.1	17.0	15.8
3α-OAc	20.7	20.7	20.7	20.7	20.7	20.6
	170.2	170.3	170.0	170.6	170.2	169.9
11α-OAc	21.2					21.4
	170.4					171.0
13α-OAc	21.4	21.4		21.4		
	169.3	169.6		169.8		
14-OAc			20.6			
			177.6			





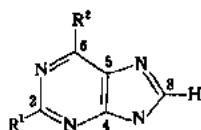
第十一节　嘌呤类生物碱的^{13}C-NMR化学位移

一、简单嘌呤衍生物的^{13}C-NMR化学位移

表 20-42　简单嘌呤衍生物 1～14 的^{13}C-NMR化学位移数据[158]①

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
2	152.10	160.59	158.31	152.69	151.76	151.30	151.57	152.37	152.42	151.76	151.91	151.50	151.52	151.72
4	154.77	155.11	158.22	157.68	153.87	155.06	150.21	151.30	150.0	151.23	151.08	154.16	152.98	150.02
5	130.46	125.52	128.79	129.06	129.59	118.14	129.40	117.61	118.2	118.97	118.46	129.23	131.97	120.18
6	145.50	147.69	147.25	146.91	155.67	159.26	158.70	155.30	154.72	154.29	153.07	147.78	140.12	136.53
8	146.09	141.62	147.98	147.79	144.51	142.59	143.13	139.29	138.76	137.74	137.86	146.18	145.94	145.02
CH_3					19.48	53.66	11.30		27.22	37.84	13.49			

① 化合物 1～14 在$(CD_3)_2SO$中测定。

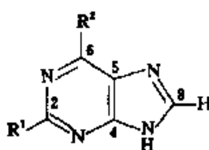


1. $R^1=R^2=H$
2. $R^1=NH_2, R^2=H$
3. $R^1=F, R^2=H$
4. $R^1=Cl, R^2=H$
5. $R^1=H, R^2=CH_3$
6. $R^1=H, R^2=OCH_3$
7. $R^1=H, R^2=SCH_3$
8. $R^1=H, R^2=NH_2$
9. $R^1=H, R^2=NHCH_3$
10. $R^1=H, R^2=N(CH_3)_2$
11. $R^1=H, R^2=N(CH_2CH_3)_2$
12. $R^1=H, R^2=Cl$
13. $R^1=H, R^2=Br$
14. $R^1=H, R^2=I$

表 20-43　简单嘌呤衍生物 15～27 的^{13}C-NMR化学位移数据[158]①

C \ 化合物	15	16	17	18	19	20	21	22	23	24	25	26	27
2	152.20	150.33	163.75	160.20	150.98	160.72	160.11	163.89	159.65	151.13	158.77	152.78	165.01
4	154.97	151.62	151.83	152.77	156.23	151.8	154.34	152.20	151.65	156.95	153.36	152.78	155.11
5	133.47	137.74	127.86	112.50	128.51	115.8	124.40	115.42	123.97	116.83	115.53	116.20	127.70
6	127.80	156.59	159.78	155.78	148.10	154.94	157.25	154.92	159.20	159.57	156.81	155.94	147.59
8	149.29	147.32	141.99	135.91	147.44	138.62	140.02	138.47	138.74	143.83	140.06	140.17	145.99
CH_3	114.43	54.27				25.33	19.02	16.63	10.80	54.70			12.61

① 化合物 15～27 在$(CD_3)_2SO$中测定。

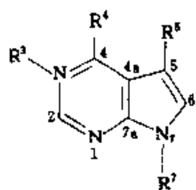


15. $R^1=H, R^2=CN$
16. $R^1=H, R^2=N(CH_3)_3^+$
17. $R^1=SCH_3, R^2=SCH_3$
18. $R^1=R^2=NH_2$
19. $R^1=R^2=Cl$
20. $R^1=CH_3, R^2=NH_2$
21. $R^1=NH_2, R^2=CH_3$
22. $R^1=SCH_3, R^2=NH_2$
23. $R^1=NH_2, R^2=SCH_3$
24. $R^1=Cl, R^2=OCH_3$
25. $R^1=F, R^2=NH_2$
26. $R^1=Cl, R^2=NH_2$
27. $R^1=CH_2CH_3, R^2=Cl$

二、吡咯并嘧啶类化合物的^{13}C-NMR化学位移

表 20-44　吡咯并嘧啶类化合物 28～38 的^{13}C-NMR化学位移数据[159]

C \ 化合物	28	29	30	31	32	33	34	35	36	37	38
2	150.8	151.0	151.1	151.6	151.3	153.7	153.0	143.3	144.0	142.8	143.5
4	148.8	149.6	157.2	157.4	157.4	157.2	158.3	158.7	158.5	176.3	176.6
4a	118.2	119.3	102.3	102.3	103.2	101.5	101.4	107.8	108.6	119.9	120.7
5	99.4	100.5	99.2	98.3	99.8	83.2	111.2	102.2	102.7	104.4	104.9
6	127.2	127.8	121.5	124.9	122.8	132.6	126.0	120.5	121.4	123.8	124.2
7a	151.2	150.7	150.0	149.9	149.5	150.3	151.1	148.2	148.0	143.6	143.4
1′		86.9			87.8	88.1	87.7		87.3		87.1
2′		74.2			73.7	74.5	74.2		74.5		74.6
3′		70.8			70.7	70.4	70.9		70.8		70.7
4′		85.3			85.1	85.7	85.6		85.3		85.4
5′		61.8			61.8	61.4	62.1		61.8		61.1



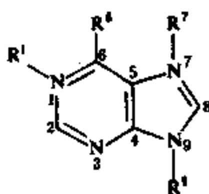
化合物	R^3	R^4	R^5	R^7	化合物	R^3	R^4	R^5	R^7
28	—	H	H	H	34	—	NH_2	$CONH_4$	核糖
29	—	H	H	核糖	35	H	O	H	H
30	—	NH_2	H	H	36	H	O	H	核糖
31	—	NH_2	H	CH_3	37	H	S	H	H
32	—	NH_2	H	核糖	38	H	S	H	核糖
33	—	NH_2	CN	核糖					

三、多取代嘌呤衍生物的^{13}C-NMR 化学位移

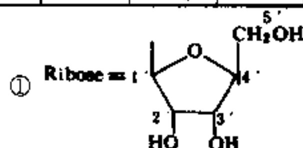
表 20-45 多取代嘌呤衍生物 39～47 的^{13}C-NMR 化学位移数据[159]①

C \ 化合物	39	40	41	42	43	44	45	46	47
CH_3	31.6	29.3		33.7		29.3		33.3	
2	152.0	151.8	152.2	152.3	152.8	152.5	152.6	144.3	144.8
4	159.8	151.3	151.0	159.8	160.7	149.9	149.2	157.0	157.7
5	125.7	133.4	134.2	111.7	110.2	118.7	119.5	115.4	114.7
6	140.7	147.4	148.3	151.9	151.7	155.9	156.3	154.6	154.1
8	149.7	147.4	145.5	145.9	144.6	141.4	140.2	144.3	142.4
1′			87.7		89.4		88.2		89.4
2′			73.9		75.0		73.7		75.1
3′			70.4		69.0		70.9		69.7
4′			85.8		86.4		86.1		85.4
5′			61.4		60.5		61.9		61.0

① 化合物 39～47 在$(CD_3)_2SO$ 中测定。



化合物	R^1	R^6	R^7	$R^9$①	化合物	R^1	R^6	R^7	$R^9$①
39	—	H	CH_3	—	44	—	NH_2	—	CH_3
40	—	H	—	CH_3	45	—	NH_2	—	Ribose
41	—	H	—	Ribose	46	H	O	CH_3	—
42	—	NH_2	CH_3	—	47	H	O	Ribose	—
43	—	NH_2	Ribose	—					

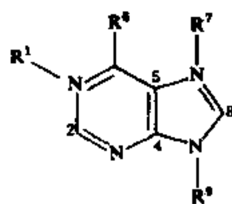
① 

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表 20-46 多取代嘌呤衍生物 48～55 的^{13}C-NMR 化学位移数据[159]①

C \ 化合物	48	49	50	51	52	53	54	55
CH_3	—	33.5	54.0	34.6	—	—	40.4	11.2
2	146.1	148.7	151.6	144.7	144.9	145.4	148.4	151.5
4	148.4	147.6	151.8	152.6	153.3	144.1	142.0	148.0
5	124.6	123.6	121.2	125.8	125.3	135.6	135.7	131.3
6	156.8	156.4	160.4	170.4	169.8	176.1	177.4	160.4
8	139.1	139.2	142.3	148.3	144.9	141.4	141.6	143.0
1′	87.8	87.5	87.8	—	89.1	87.9	87.6	88.0
2′	74.4	74.2	73.8	—	75.7	74.5	74.3	73.9
3′	70.5	70.4	70.5	—	68.9	70.4	70.2	70.3
4′	85.9	85.7	85.8	—	84.6	85.9	85.7	85.8
5′	61.5	61.4	61.4	—	60.3	61.3	61.2	61.3

① 化合物 48～55 在$(CD_3)_2SO$ 中测定。

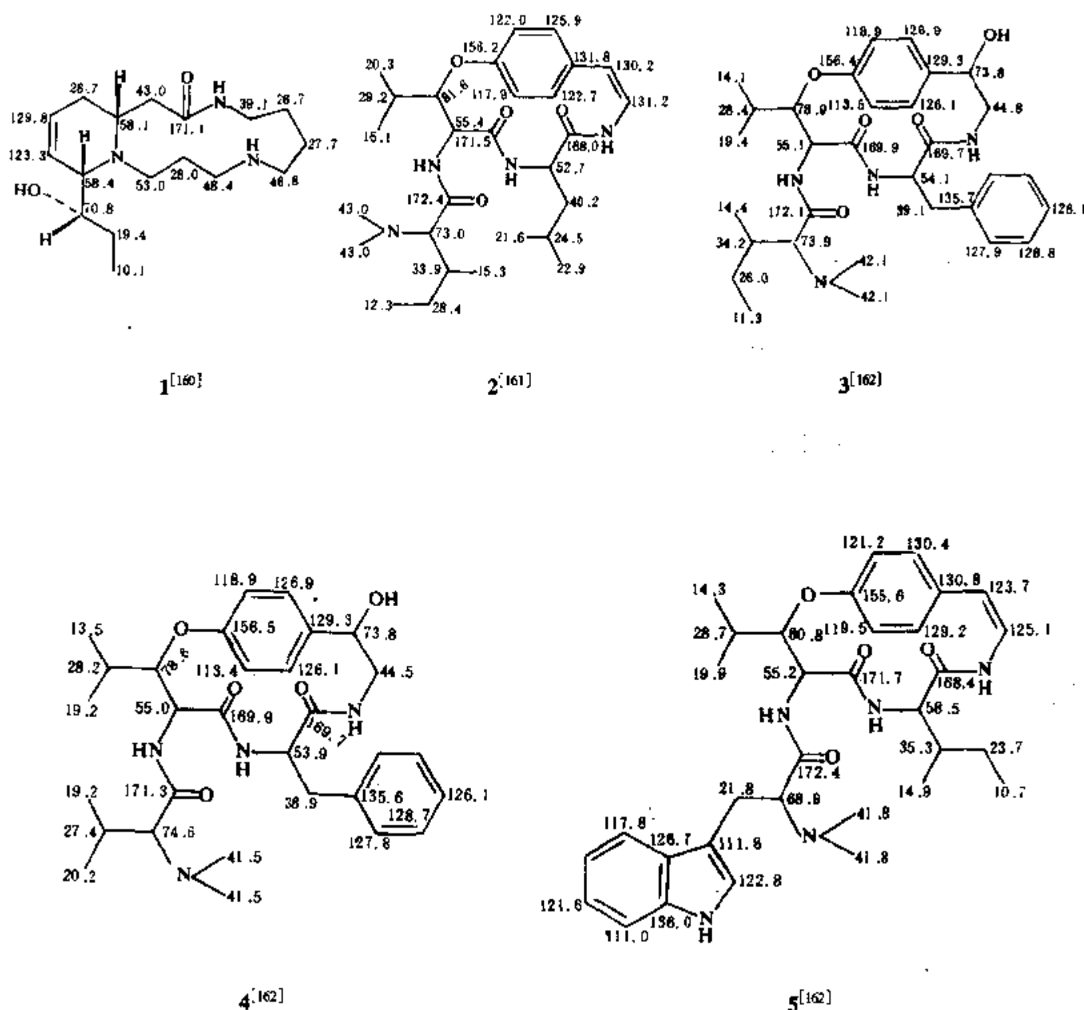


化合物	R¹	R⁶	R⁷	R⁹①	化合物	R¹	R⁶	R⁷	R⁹①
48	H	O	—	Ribose	**52**	H	S	Ribose	—
49	CH_3	O	—	Ribose	**53**	H	S	—	Ribose
50	—	OCH_3	—	Ribose	**54**	CH_3	S	—	Ribose
51	H	S	CH_3	—	**55**	—	SCH_3	—	Ribose

① 见表 20～39 下面所注。

第十二节　环肽及其他生物碱的^{13}C-NMR 化学位移

一、环肽生物碱的^{13}C-NMR 化学位移❶



1[160]　**2**[161]　**3**[162]

4[162]　**5**[162]

❶ 化合物 3～9 在 $CDCl_3 + CH_3OH(2+1)$中测定。

6[162]

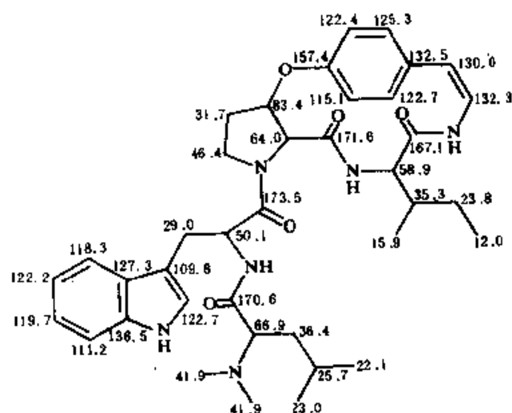
7[162]

8[162]

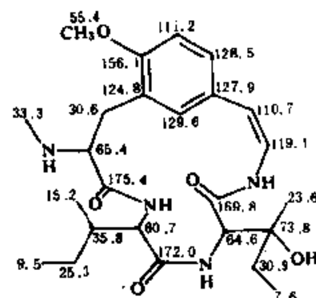
9[162]

10[163]

11[163]



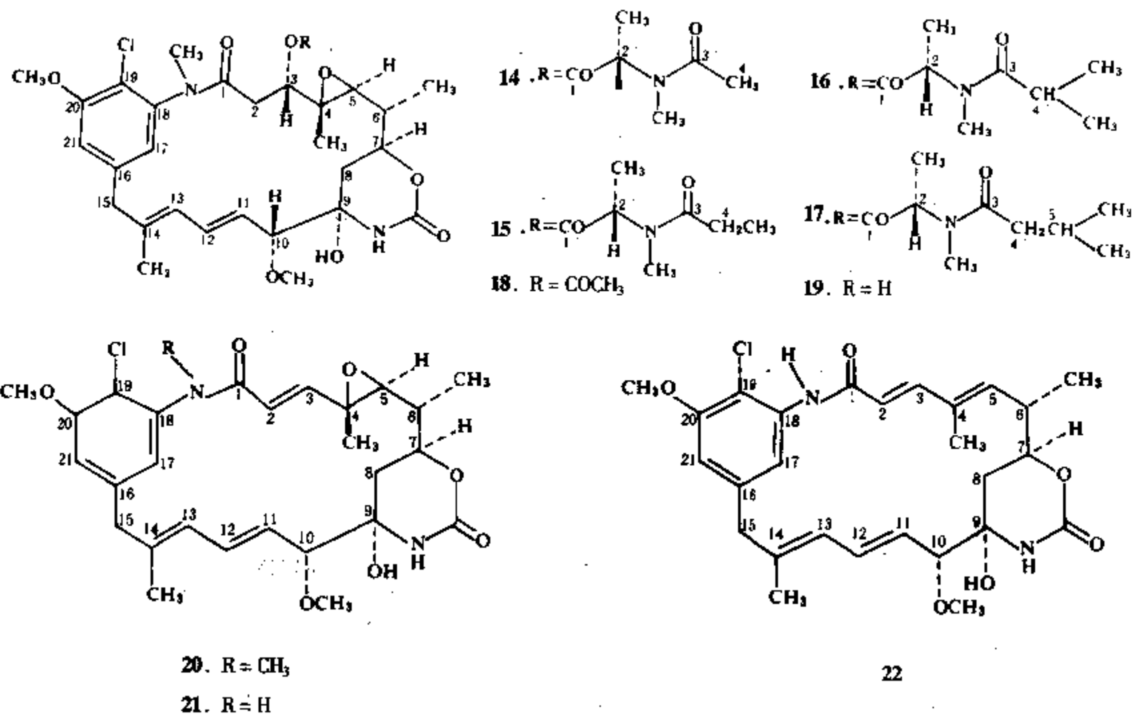
12[163]



13[163]

表 20-47 美登木生物碱 14～22 的 ^{13}C-NMR 化学位移数据

C \ 化合物	14	15	16	17	18	19	20	21	22
2	32.5	32.5	32.5	32.6	32.8	35.6	121.9	118.8	116.9
3	78.2	78.1	78.2	78.2	77.0	75.8	147.5	150.0	148.0
4	60.1	60.1	60.1	60.1	60.3	63.1	59.7	59.8	135.0
5	67.2	67.2	67.3	67.2	66.4	66.6	66.9	66.9	140.9
6	39.1	39.0	39.1	39.1	38.5	37.9	38.7	39.1	39.2
7	74.2	74.2	74.3	74.2	74.3	75.4	75.0	74.8	75.5
8	36.5	36.4	36.5	36.4	36.0	35.8	35.5	35.8	35.5
9	81.0	81.0	81.0	81.0	81.1	81.3	81.2	81.1	81.0
10	88.9	88.8	88.9	88.9	88.3	89.0	88.6	88.5	88.3
11	127.8	127.9	127.8	127.8	128.3	127.1	127.2	127.9	128.0
12	133.3	133.3	133.4	133.3	132.2	133.3	133.0	132.4	132.5
13	125.4	125.6	125.6	125.5	124.5	125.2	124.6	125.8	125.5
14	139.1	139.0	139.1	139.1	139.9	138.9	140.3	139.2	139.3
15	46.7	46.5	46.5	46.6	47.2	47.1	46.7	46.6	47.2
16	142.4	142.3	142.3	142.4	142.7	142.5	142.0	139.6	138.9
17	122.5	122.4	122.9	122.7	122.2	123.7	122.2	120.8	118.0
18	141.2	141.2	141.1	141.1	140.1	140.2	140.5	135.7	136.4
19	119.1	119.0	119.1	119.2	119.0	119.0	119.3	115.6	114.4
20	156.1	156.1	156.1	156.1	156.2	155.8	156.4	156.0	155.8
21	113.4	113.4	113.5	113.5	113.1	112.9	112.7	111.4	111.0
C=O	152.2	152.2	152.2	152.1	152.2	152.7	152.1	152.4	152.5
C=O	168.8	168.7	168.8	168.7	168.7	171.8	164.3	164.6	166.3
C=O	170.2	171.0	171.1	171.0	169.1				
C=O	170.8	173.3	176.7	172.2					
4-CH$_3$	12.2	12.2	12.2	12.2	12.1	11.3	14.2	14.3	13.7
6-CH$_3$	14.5	14.5	14.6	14.5	14.5	14.5	14.8	14.9	15.7
14-CH$_3$	15.5	15.4	15.5	15.5	15.8	15.8	16.0	16.0	16.8
10-OCH$_3$ 20-OCH$_3$	56.7	56.6	56.6	56.6	56.7	56.6	56.6 56.7	56.6	56.6
18-NCH$_3$	35.4	35.3	35.3	35.4	35.6	36.0	36.0		
2′	52.2	52.3	52.6	52.6	20.9				
2′-CH$_3$	13.4	13.3	13.3	13.5					
2′-NCH$_3$	31.7	30.6	30.7	31.2					
4′	21.7	26.7	30.5	42.5					
4′-CH$_3$		9.1	18.9 19.5						
5′				25.6					
5′-CH$_3$				22.8 25.6					



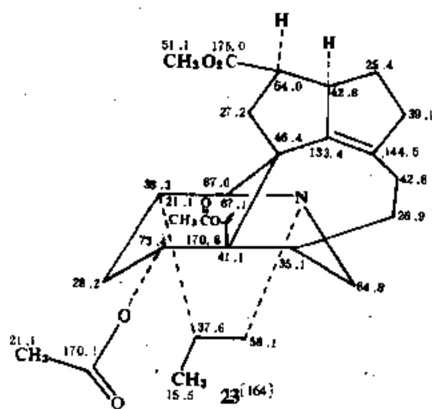
18. R = $COCH_3$ 19. R = H

20. R = CH_3

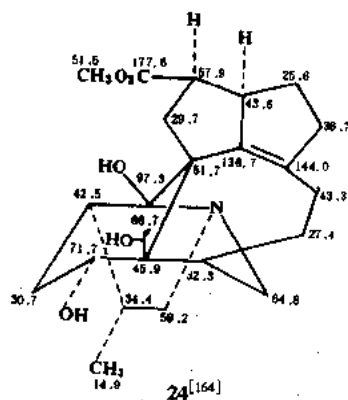
21. R = H

22

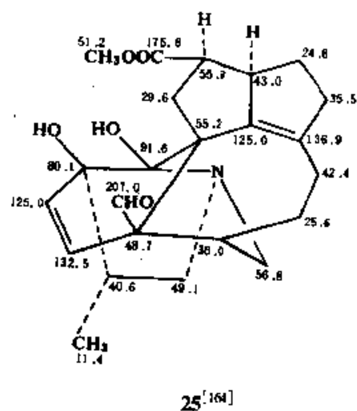
二、交让木生物碱的^{13}C-NMR化学位移



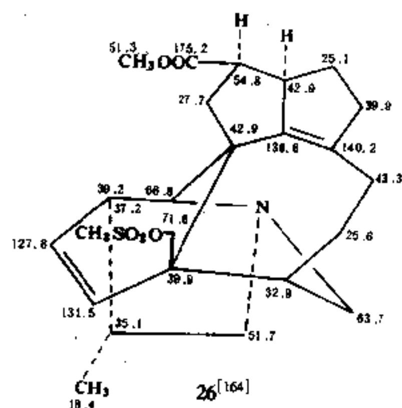
23[164]



24[164]



25[164]



26[164]

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第二十一章　萜类化合物的^{13}C-NMR化学位移

第一节　概　述

萜类化合物包括单萜、倍半萜、二萜、二倍半萜、三萜、四萜和多萜以及其甙类，每种萜类化合物又分为直链、单环、双环、三环、四环和多环，根据构成其分子的结构骨架又可分成各种不同类型，因此各种萜类化合物的^{13}C-NMR化学位移也各不相同。

1. 一般的萜类化合物的^{13}C-NMR化学位移特征

（1）不同类型的碳的化学位移　在一般情况下，CH_3的化学位移为10～30，CH_2为20～45，CH为25～55，季碳为30～55，烯属碳为105～165，炔碳为65～95，与氧连接的碳（包括醇或醚）为50～100，而羰基碳为180～220。

（2）几何异构体的化学位移　萜类化合物，尤其是直链萜往往由于双键的存在而有几何异构体，在这些几何异构体中，由于γ-效应碳中间反式甲基的化学位移一般比顺式甲基的化学位移处于高场，其他邻近构型的碳的化学位移也有一定的变化。

（3）骨架上不同的取代基的化学位移　在萜类化合物骨架上不同的取代基的化学位移效应是不同的。

2. 几种化学位移规律特征较强的萜类化合物

（1）环烯醚萜或其甙类的^{13}C-NMR化学位移特征

① 对于一般的环烯醚萜甙来说C_1-OH与葡萄糖成甙，C-1化学位移在95～104左右，如果C_5位存在羟基时，其化学位移约在71～74，如果C-6位存在羟基时，其化学位移约在75～83，C-7一般情况下没有羟基，如果C-7位存在羟基时，其化学位移在75左右，如果C-8位存在羟基时，其化学位移约在62左右。C_{10}位甲基通常为羟甲基或羧基化，如果C-10为羟甲基其化学位移为66左右，若C-7有双键，其化学位移为61左右。C-10为羧基时，其化学位移在175～177之间。C-11位通常为羧酸甲酯或羧基、醛基状态，如为醛基时，化学位移在190左右，为羧基时，化学位移在170～175之间，如果形成羧酸甲酯，其化学位移在167～169左右。环烯醚萜绝大多数有$\Delta^{3(4)}$，由于2位氧的影响，C-3比C-4处于低场。如果分子中C-7位和C-8位之间有双键，且同时C-8位有羟甲基取代，则C-7化学位移比C-8的化学位移处于高场，而如果C-8位有羧基取代，则C-7比C-8处于低场。有的化合物C-6为羰基，其化学位移在212～219之间。

② 4-去甲基环烯醚萜甙的^{13}C-NMR化学位移，由于4位去掉甲基，所以C-4化学位移一般在143～139，C-3在102～111之间。

③ 8-去甲基环烯醚萜甙的^{13}C-NMR化学位移，由于8位去掉甲基，如果有$\Delta^{7(8)}$时，其化学位移在134～136左右，如果C-7和C_8与氧形成含氧三元环，其化学位移一般在56～60之间。

（2）三萜及其甙的^{13}C-NMR化学位移特征

① 四环三萜主要是达玛烷型，其C-3有β-OH时，C-3的化学位移在78.4～78.9左右，C-3有α-OH时，C-3的化学位移在75.9～76.1左右。C-12有β-OH时，C-12的化学位移在

70.5～70.8 左右，有 α-OH 时，其化学位移在 68.4 左右。C-6 位有 α-OH 时，C-6 的化学位移在 68.4 左右。C-20 位有 α-OH 和 β-OH 时，对 C-20 的化学位移影响相同，约在 73.5～75.6 之间。侧链 C-24、C-25 之间多数有双键，C-24 的化学位移在 124.6～125.3，C-25的化学位移在 131.2～131.9 左右。若 C-3 羟基变成羰基，则 C-3 的化学位移在 217.6～217.7。

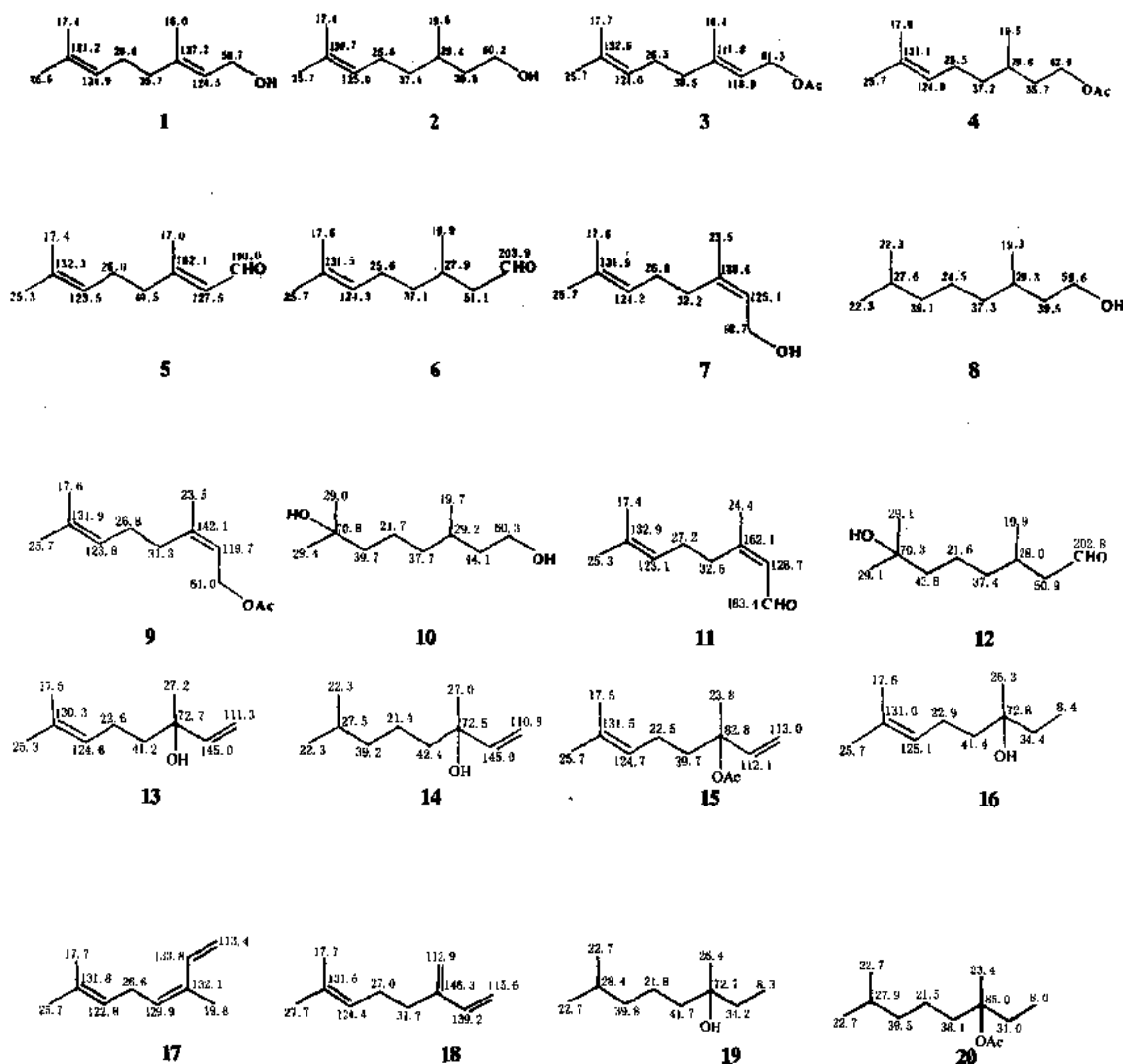
② C-20～C-24 氧呋喃达玛烷型三萜，C-24（S）的化学位移在低场，约 88.4 左右，C-24（R）的化学位移在高场，约在 85.6～85.7 左右。

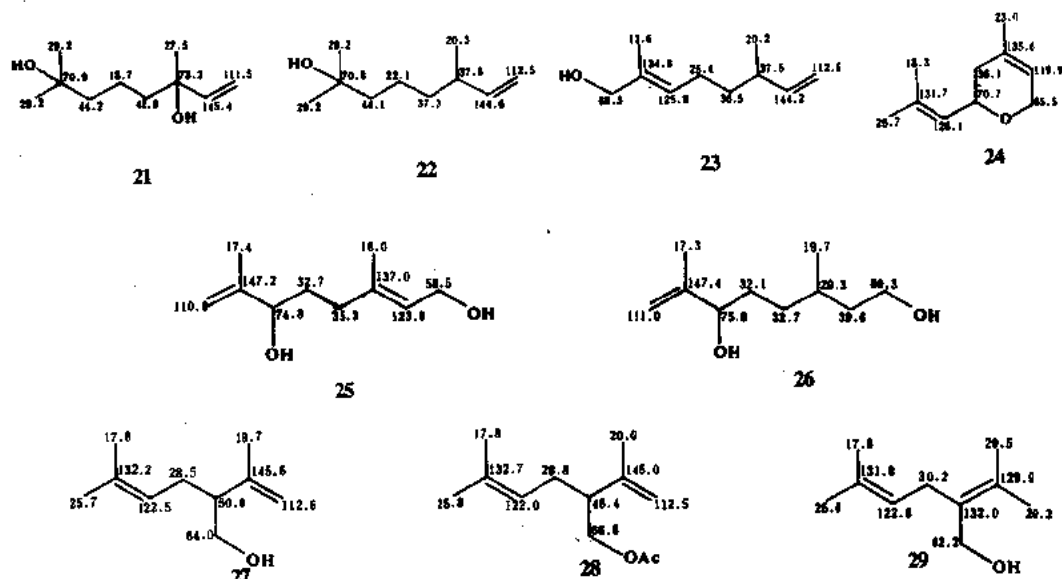
③ 齐墩果烷型三萜，多数情况下在 C-12、C-13 位之间有双键，C-12在高场，约为 122.3～123.0，C-13 在低场，约为 143～145。C-28 位多数为羧基，其化学位移在 180 左右。母核中 23、27、29 位的 α-甲基比 24、25、28、30 位的 β-甲基处于低场。

④ 羽扇豆烷型三萜多数有 C-20、C-30 双键，C-20的化学位移为 150.5～150.9，C-30 的化学位移在 109.3～109.7 左右。

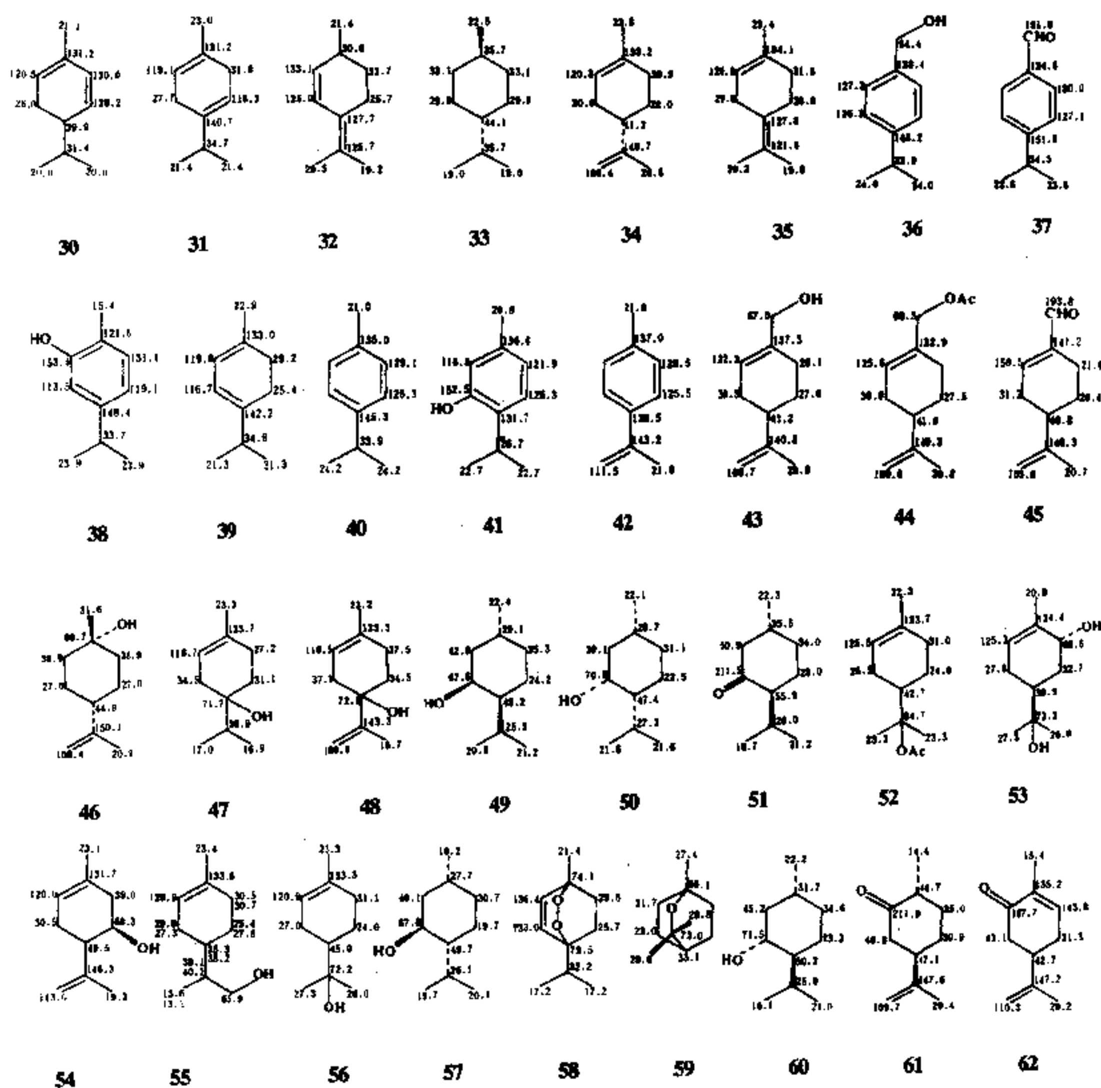
第二节　单萜类化合物的^{13}C-NMR 化学位移

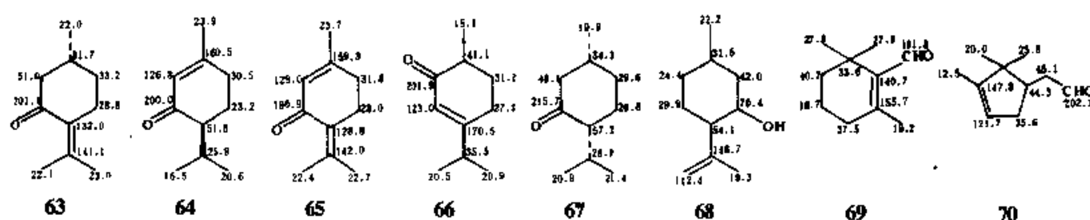
一、非环单萜的^{13}C-NMR 化学位移[1]



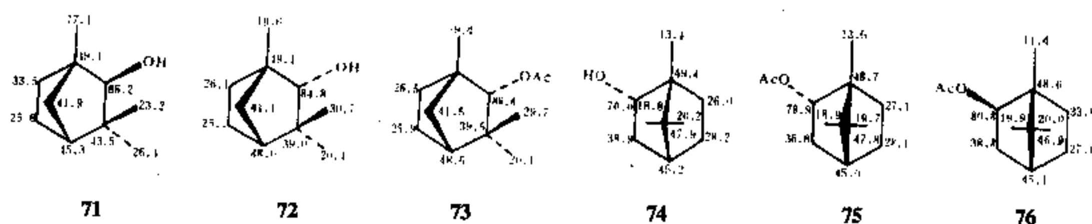


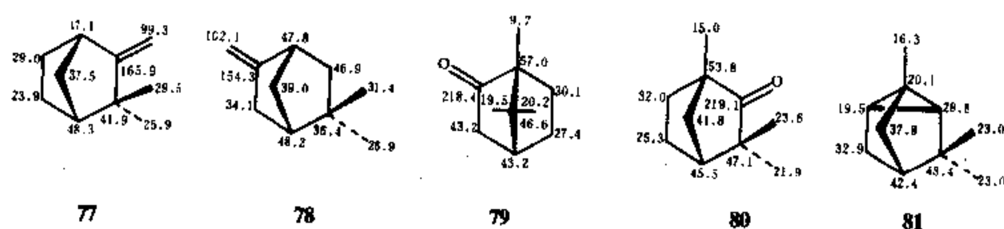
二、单环单萜化合物的13C-NMR化学位移[1]

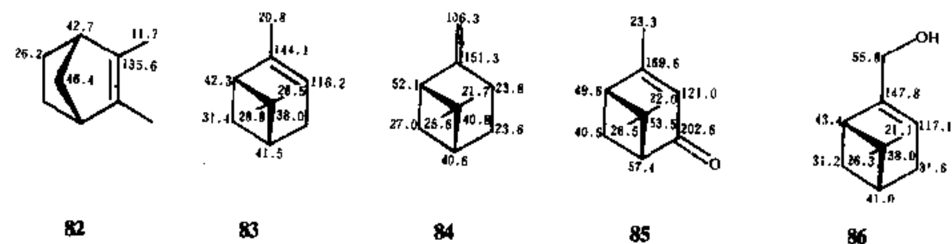


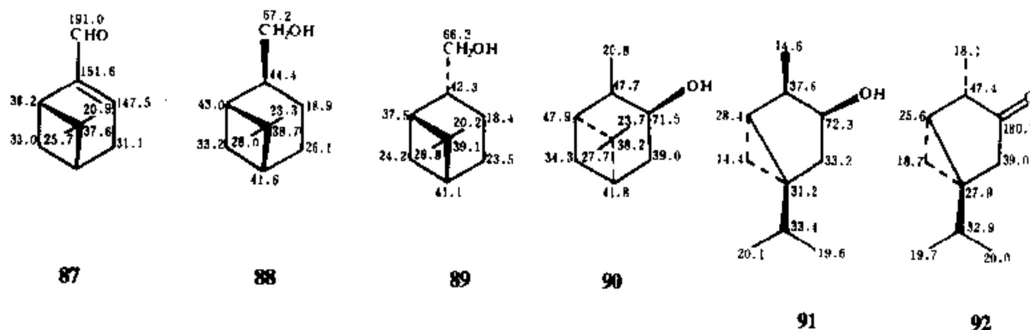


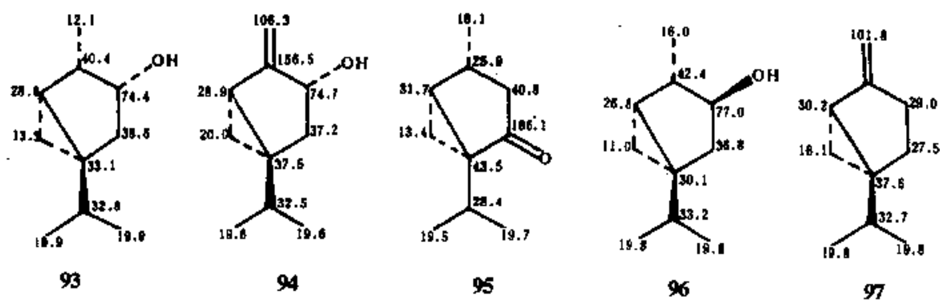
三、双环单萜化合物的^{13}C-NMR化学位移[2]

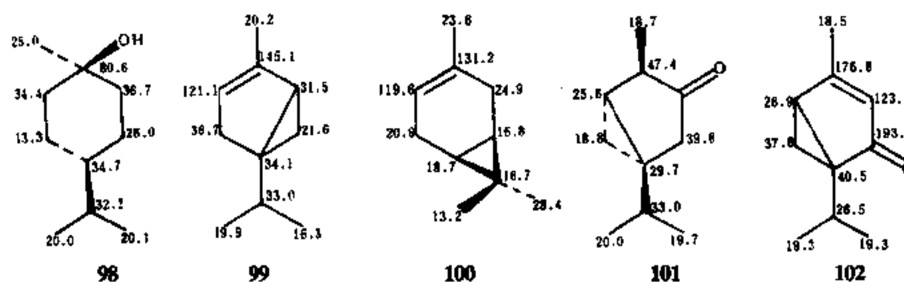












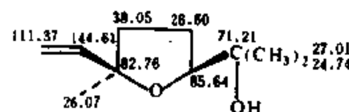
98 99 100 101 102

四、单萜甙和环醚单萜化合物的^{13}C-NMR化学位移

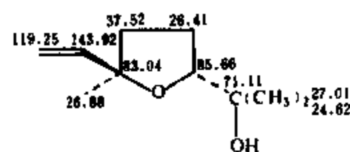
表 21-1 单萜甙类化合物 103～104 的^{13}C-NMR化学位移数据[3]①

C \ 化合物	103	104	结构
1	88.9	91.3	
2	86.1	86.3	
3	44.8	41.8	
4	106.0	67.4	
5	43.9	41.4	
6	71.7	56.1	
7	23.5	28.3	
8	61.5	61.7	
9	101.7	175.7	
10	19.9	20.7	
1′	100.5	100.3	
2′	74.7	74.8	
3′	78.4	78.4	
4′	71.7	71.6	
5′	78.4	78.4	
6′	62.9	62.8	
1″	130.6	130.8	103　104
2″, 6″	129.9	130.1	
3″, 5″	128.8	128.7	
4″	133.3	133.2	
7″	166.6	166.6	

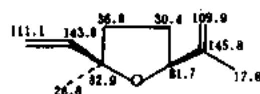
① 以 C_5D_5N 为溶剂。



105[4]



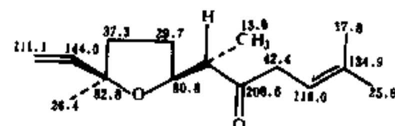
106[4]



107[4]



108[4]

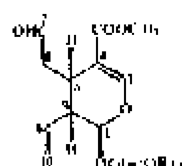
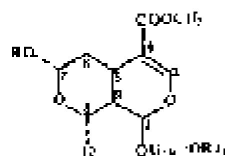
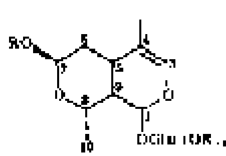
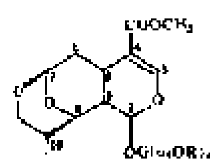
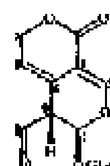


109[4]

五、环烯醚萜甙的^{13}C-NMR化学位移

表 21-2 环烯醚萜甙 110～118 的^{13}C-NMR化学位移数据[5]

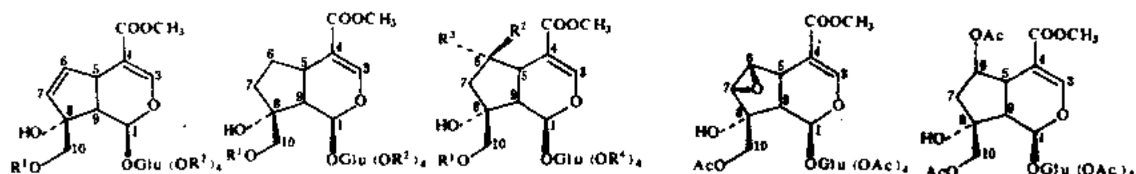
C \ 化合物	110	111	112	113	114	115	116	117	118
1	97.6	95.4	96.2	94.5	96.2	94.2	96.3	95.7	98.5
3	154.0	150.7	154.9	151.9	154.9	151.9	151.1	152.2	150.4
4	109.6	109.1	110.2	109.9	110.9	110.7	109.8	109.7	104.4
5	27.5	25.1	31.1	30.0	26.8	26.1	25.2	24.6	125.2
6	44.6	43.5	36.1	32.9	33.4	31.4	34.6	34.4	117.8
7	206.8	199.7	95.9	93.5	91.6	91.1	103.3	103.8	71.2
8	133.8	130.8	73.8	75.3	65.9	67.1	76.9	77.2	133.9
9	44.6	43.1	38.7	36.8	39.3	39.2	37.2	36.8	45.4
10	121.6	120.6	19.6	18.8	19.6	18.8	96.7	95.1	119.5
C=O	169.8	166.1	169.8	165.8	169.8	165.9	169.5	166.6	167.5
OCH_3	52.0	51.3	52.6	51.2	52.6	51.1	52.7	51.3	
1'	99.6	95.4	99.5	96.5	99.5	96.6	100.4	98.4	99.6
2'	73.5	70.4	73.6	70.8	73.6	70.9	73.6	71.0	73.3
3'	76.6	72.0	76.8	72.4	76.8	72.5	76.7	72.7	76.5
4'	70.5	67.9	70.5	68.3	70.5	58.4	70.4	68.4	70.9
5'	77.2	72.0	77.1	71.8	77.1	72.0	77.1	72.1	77.1
6'	61.6	61.4	61.6	61.6	61.6	61.5	61.6	61.9	61.6

110. R=H 111. R=Ac　112. R=H 113. R=Ac　114. R=H 115. R=Ac　116. R=H 117. R=Ac　118

表 21-3 环烯醚萜甙 119～128 的^{13}C-NMR化学位移数据[6]

C \ 化合物	119	120	121	122	123	124	125	126	127	128
1	95.0	95.0	94.2	96.0	95.5	98.2	92.3	95.1	94.8	91.6
3	151.9	151.9	150.0	153.0	152.6	150.8	151.6	153.6	153.5	151.7
4	111.0	110.8	110.9	112.2	112.6	111.3	106.8	109.8	109.3	108.0
5	37.7	37.6	37.8	33.6	32.4	35.2	31.6	40.4	40.2	37.7
6	132.7	131.8	131.8	30.6	30.1	30.7	59.0	76.3	75.9	76.7
7	137.9	138.3	137.7	36.0	36.3	36.7	58.3	44.0	44.2	42.3
8	85.5	83.8	83.4	82.9	80.9	80.4	77.6	81.7	80.0	78.3
9	44.7	45.7	45.1	45.7	46.6	45.1	42.7	44.5	45.2	43.9
10	67.1	70.7	69.5	68.6	71.0	70.2	68.1	69.0	72.0	70.8
11	170.2	170.0	166.6	170.4	170.6		166.1	170.4		166.2
OCH_3	52.6	52.6	51.4	52.6	52.5	51.2	51.2	52.7	52.6	51.3
1'	99.0	99.0	96.3	99.8	99.4	96.3	95.0	99.2	99.0	96.1
2'	73.3	73.4	70.7	73.5	73.4	70.4	70.3	73.4	73.3	70.3
3'	76.3	76.4	72.4	76.5	76.3	72.1	72.1	76.3	76.3	72.1
4'	70.3	70.3	68.3	70.3	70.2	68.0	67.8	70.3	70.2	67.8
5'	76.9	76.9	72.4	77.1	77.0	72.1	72.1	77.0	77.0	72.1
6'	61.4	61.4	61.8	61.5	61.4	61.4	61.4	61.4	61.4	61.4



119. $R^1=R^2=H$ **120.** $R^1=Ac$，$R^2=H$ **121.** $R^1=R^2=Ac$

122. $R^1=R^2=H$ **123.** $R^1=Ac$，$R^2=H$ **124.** $R^1=R^2=Ac$

126. $R^1=R^3=R^4=H$，$R^2=OH$ **127.** $R^1=Ac$，$R^2=OH$ $R^3=R^4=H$

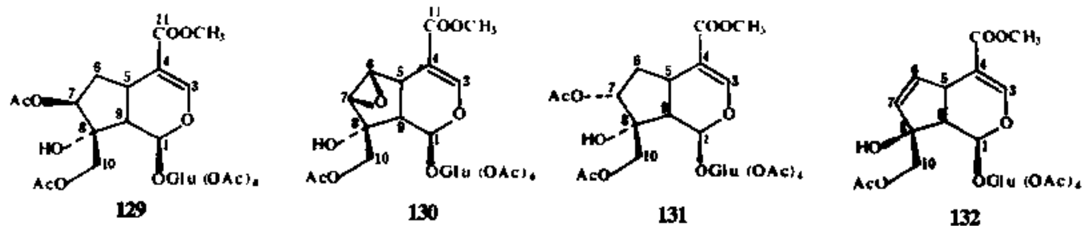
125

128

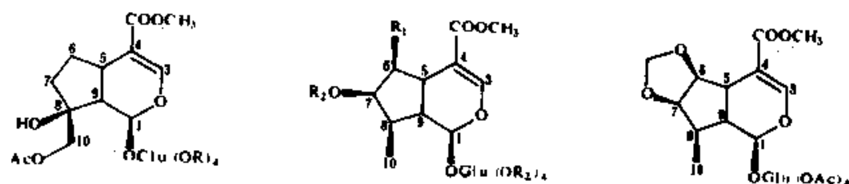
表 21-4　环烯醚萜甙 129～137 的¹³C-NMR 化学位移数据[6]

C \ 化合物	129	130	131	132	133	134	135	136	137①
1	94.1	98.6	93.1	92.1	95.1	93.5	97.4	94.0	93.8
3	150	152.5	149.6	148.9	152.3	150.0	153.1	150.6	150.5
4	111.4	104.5	112.2	110.8	112.3	112.4	111.3	109.9	109.6
5	29.7	36.4	27.5	36.9	32.3	31.9	38.4	35.5	38.5*
6	35.9	60.0	34.9	133.5	29.3	28.9	79.5	76.8	83.0*
7	80.2	56.1	74.8	134.9	34.1	34.8	75.1	74.6	81.6*
8	80.6	79.3	78.1	83.1	83.5	80.8	37.9	35.1	37.6*
9	44.4	39.4	43.2	50.5	50.3	50.0	44.7	44.5	42.7
10	66.3	67.3	66.5	67.6	65.9	67.9	13.4	13.1	11.6
11	166.5	166.6		166.1		167.0	170.8	166.2	
OCH_3		51.4	51.1	51.0	52.5	51.2	52.8	51.3	51.3
1′	96.6	99.2	96.1	95.1	99.2	96.0	99.4	95.7	95.4
2′	70.2	70.8	70.3	70.3	73.3	70.6	73.5	70.4	70.3
3′	72.0	72.4	72.0	71.9	76.3	72.2	76.5	72.1	72.0
4′	67.9	68.2	67.9	67.8	70.2	68.2	70.4	68.0	67.9
5′	72.0	72.4	72.0	72.2	77.0	72.5	77.2	72.2	72.3
6′	61.4	61.4	61.4	61.4	61.4	61.4	61.6	61.5	61.5

① 带 "*" 的相近数据是可以互换的。



129　**130**　**131**　**132**



133. R＝H
134. R＝Ac

135. $R^1=OH$，$R^2=H$
136. $R^1=OAc$，$R^2=Ac$

137

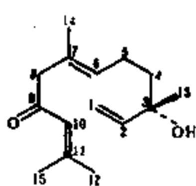
第三节　倍半萜类化合物的^{13}C-NMR 化学位移

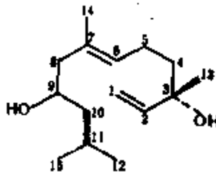
一、一般倍半萜化合物的^{13}C-NMR 化学位移

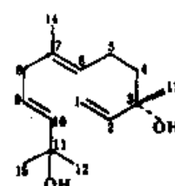
1. 简单倍半萜的^{13}C-NMR 化学位移

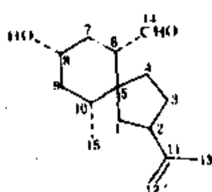
表 21-5　倍半萜 1～6 的^{13}C-NMR 化学位移数据[7]

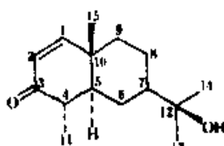
C \ 化合物	1	2	3	4	5	6	C \ 化合物	1	2	3	4	5	6
1	111.6	111.8	111.7	33.3	160.9	156.7	8	55.2	48.1	42.4	69.3	22.4	23.9
		(111.7)					9	198.9	66.0	125.2	40.3	40.0	41.0
2	144.8	144.9	144.9	41.0	125.9	128.5	10	129.2	128.5	139.4	47.4	36.2	38.2
		(145.1)							(128.4)				
3	73.2	73.5	73.4	32.6	204.0	201.9	11	155.4	131.8	70.6	147.3	13.4	12.0
		(73.4)							(131.9)				
4	41.8	41.8	42.1	25.9	49.1	48.6	12	27.6	25.7	29.9	108.8	72.6	72.7
5	23.0	23.0	22.9	46.9	45.3	48.5	13	27.9	28.0	27.9	21.2	27.2	27.1
		(22.9)							(28.2)				
6	122.8	127.7	125.0	58.4	26.1	24.5	14	16.4	16.2	16.2	204.9	27.6	27.1
7	129.6	134.8	134.1	41.8	44.5	42.1	15	20.7	18.2	29.9	16.4	20.8	27.1

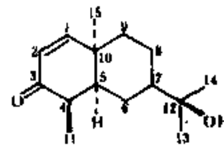

1

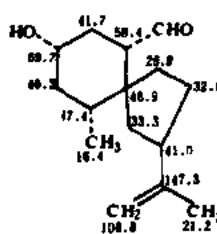

2

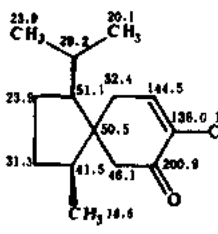

3

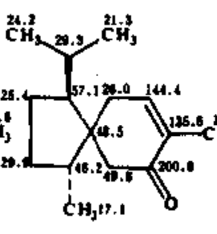

4

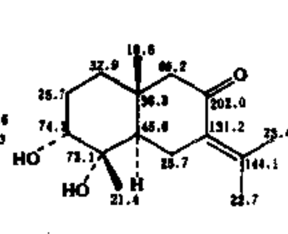

5

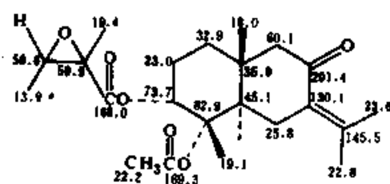

6


7[7]

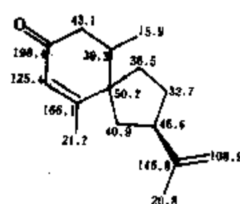

8[8]


9[8]

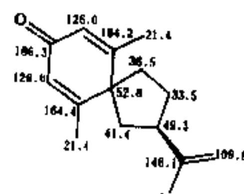

10[9]



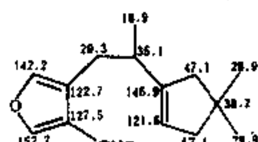
11[9]

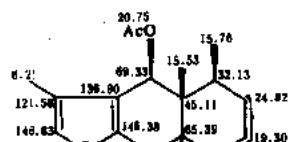


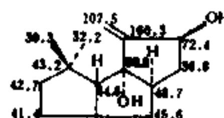
12[10]

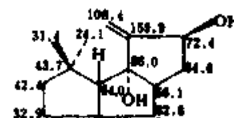


13[10]









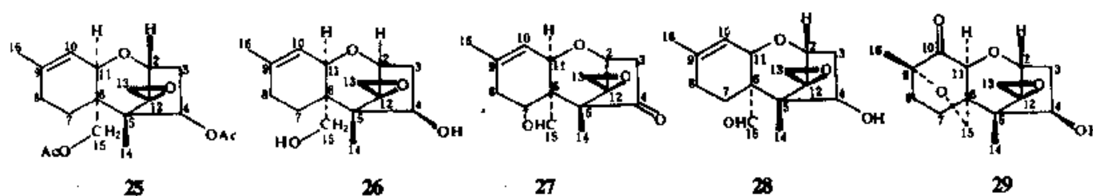
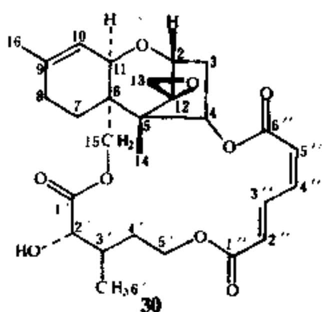
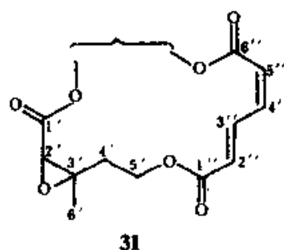
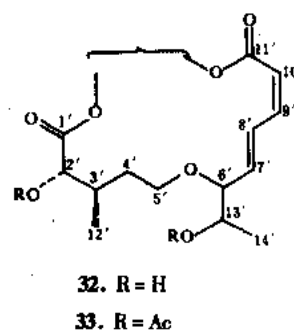

25　26　27　28　29

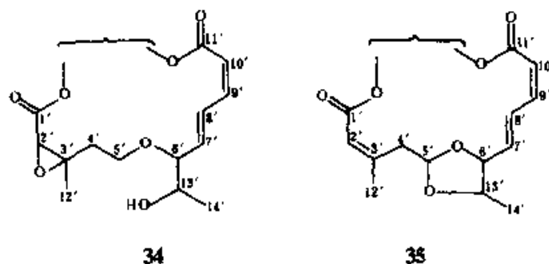
表 21-7　单端孢菌烷及其衍生物 30～35 的^{13}C-NMR 化学位移数据[17]

C \ 化合物	30	31	32	33	34	35
2	78.6	78.7	78.8	78.8	78.8	79.0
3	34.6	34.8	34.6	34.6	34.9	34.8
4	75.3	75.4	74.2	74.3	74.3	74.0
5	49.2	49.0	49.1	49.1	49.0	48.9
6	43.9	43.6	43.6	43.7	43.1	43.2
7	19.7	19.8	20.0	20.7	20.4	20.5
8	27.2	27.4	27.5	27.2	27.4	27.6
9	140.7	140.4	140.4	140.7	140.1	139.9
10	117.7	118.0	118.2	119.9	118.4	118.6
11	66.6	66.9	66.9	67.0	66.9	67.6
12	64.9	64.9	64.9	64.9	65.1	65.3
13	47.4	47.5	47.4	47.4	47.4	47.3
14	7.0	7.3	7.2	6.9	6.8	7.0
15	63.1	63.6	64.2	63.3	64.3	63.0
16	22.9	22.8	22.9	22.9	22.9	22.9
1′	174.3	167.4	174.5		167.8	166.0
2′	73.8	58.0	75.3	76.6	57.9	119.0
3′	32.9	61.1	36.7	32.9	62.9	154.4
4′	31.9	36.9	33.0	33.7	39.4	47.7
5′	60.8	60.4	69.5	68.2	67.3	100.8
6′	9.8	15.8	83.7	79.1	85.3	81.9
1″	165.8	165.8	C (7′) 139.0	137.6	138.1	134.6
2″	127.2	127.2	C (8′) 126.0	126.9	126.2	126.2
3″	138.6	138.0	C (9′) 143.6	142.8	142.9	142.4
4″	138.6	138.0	C (10′) 117.2	117.6	117.8	118.9
5″	125.5	125.6	C (11′) 166.3	166.3	166.1	166.0
6″	165.1	164.9	C (12′) 14.4	14.6	17.2	18.2
			C (13′) 70.4	70.5	70.5	76.8
			C (14′) 18.0	14.1	17.9	16.3
			CH_3 (Ac)	20.1		


30


31


32. R = H
33. R = Ac



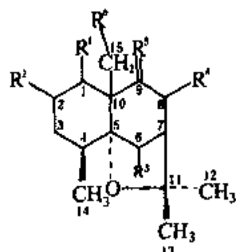
34　　　35

3. 四氢呋喃型倍半萜的^{13}C-NMR 化学位移

表 21-8　四氢呋喃倍半萜 36～45 的^{13}C-NMR 化学位移数据[18]

C \ 化合物	36	37①	38	39	40	41	42	43	44①	45
1	69.7	71.8	71.8	71.6	71.2	71.0	76.8	69.7	71.6	80.0
2	25.7	22.2	22.6	23.5	22.4	26.0	25.3	26.0	22.6	73.4
3	27.4	26.7	26.5	26.6	25.8	27.6	27.2	27.6	26.6	36.3
4	40.0	39.3	39.6	39.4	39.4	33.5	33.7	33.6	33.6	40.9
5	87.4	88.6	86.3	89.4	89.0	91.3	92.0	91.3	90.8	88.0
6	35.6	36.1	36.4	36.6	37.2	74.8	74.6	74.1	76.1	30.3
7	50.5	48.2	48.1	50.4	48.7	58.1	56.4	57.8	53.5	51.1
8	71.7	74.6	72.2	77.5	77.1	74.8	73.2	71.4	73.5	73.0
9	69.8	69.0	68.2		199.8	71.4	79.3	70.0	69.5	66.1
10	51.9	51.1	50.9	64.3	60.9	53.1	45.7	52.8	51.9	47.9
11	80.9	82.9	81.9	83.4	83.7	80.2	81.5	80.9	83.2	80.1
12	25.7	24.9	24.5	24.9	24.7	26.4	26.1	26.0	26.6	24.5
13	31.8	30.4	31.2	30.4	30.0	31.5	31.8	31.9	30.9	30.8
14	17.2	16.7	17.1	15.0	15.0	17.6	17.5	17.4	16.4	17.8
15	61.3	63.2	63.7	62.3	61.5	62.9	10.9	63.8	63.8	18.6

① 化合物 37，44 在 $(CD_3)_2SO$ 中测定。



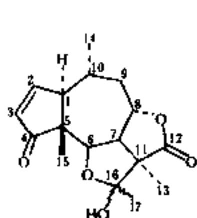
化合物	R¹	R²	R³	R⁴	R⁵	R⁶
36	β-OH	H	H	α-OH	H，α-OH	OH
37	β-OAc	H	H	α-OAc	H，α-OH	OAc
38	β-OAc	H	H	α-OAc	H，α-OAc	OAc
39	β-OH	H	H	α-OH	O	OH
40	β-OAc	H	H	α-OAc	O	OAc
41	β-OH	H	α-OH	β-OH	H，α-OH	OH
42	β-OH	H	α-OH	α-OH	H，β-OH	H
43	β-OH	H	α-OH	α-OH	H，α-OH	OH
44	β-OAc	H	α-OAc	α-OAc	H，α-OH	OAc
45	β-OH	α-OH	H	β-OH	H，α-OH	H

二、倍半萜内酯的^{13}C-NMR 化学位移

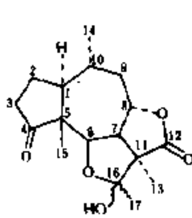
1. 愈创木烷型内酯的^{13}C-NMR 化学位移

表 21-9　愈创木烷型内酯 46～55 的^{13}C-NMR 化学位移数据[16]

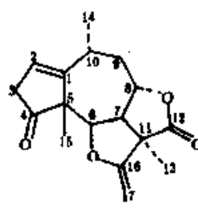
C \ 化合物	46	47	48	49	50	51	52	53	54	55
1	54.3	54.7	48.3	48.6	150.1	48.4	52.7	47.3	173.2	47.8
2	162.6	162.3	24.7	24.2	122.7	24.4	161.1	24.3	138.4	23.0
3	130.4	130.0	34.6	34.5	39.7	34.4	130.3	35.1	207.0	35.8
4	212.7	212.3	221.6	221.2	217.6	220.3	210.6	219.8	37.2	209.7
5	56.3	55.3	54.5	53.4	53.4	53.4	54.5	54.3	44.0	64.0
6	77.4	74.0	78.4	74.8	78.6	49.1	66.0	67.5	66.0	201.6
7	63.3	63.8	61.7	62.0	60.2	59.6	55.1	53.6	58.4	61.8
8	76.5	76.0	76.1	75.6	75.5	75.3	75.8	75.9	75.8	76.5
9	42.9	42.5	42.4	42.0	41.3	41.8	44.7	44.9	38.1	44.9
10	28.4	28.0	30.8	30.3	291.8	30.3	27.2	29.5	31.3	29.2
11	58.8	58.8	58.5	58.3	56.5	54.4	37.0	37.0	41.2	36.8
12	176.4	176.42	175.6	177.6	175.4	75.4	177.4	177.6	178.0	177.2
13	18.3	19.0	18.0	18.5	21.2	21.3	20.6	20.6	20.6	20.1
14	19.6	20.4	13.7	13.8	16.2	13.7	19.7	14.8	8.12	14.8
15	19.9	20.4	19.8	19.6	19.2	19.7	13.9	13.8	12.0	18.7
16	108.4	105.2	107.6	104.4	161.4	162.0	169.2	169.2		
17	24.7	27.3	24.6	26.8	83.7	82.7	20.0	19.8		



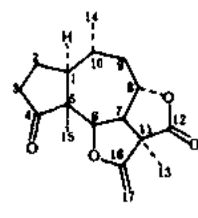
46. C-17α-CH_3
47. C-17β-CH_3



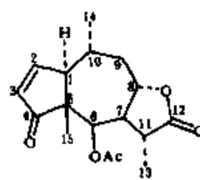
48. C-17α-CH_3
49. C-17β-CH_3



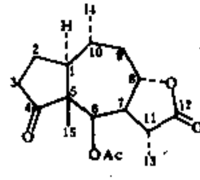
50



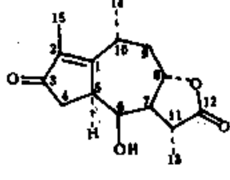
51



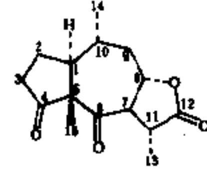
52



53



54

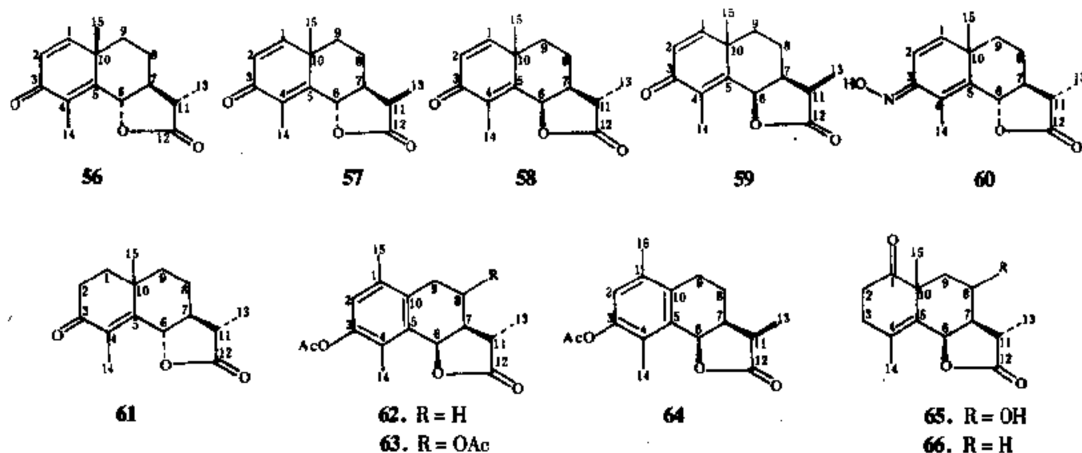


55

2. 桉烷型内酯的^{13}C-NMR 化学位移

表 21-10　桉烷型内酯 56～66 的^{13}C-NMR 化学位移数据[19]

C \ 化合物	56	57	58	59	60	61	62	63	64	65	66
1	155.1	155.0	157.5	157.6	42.1	145.6	—	—	—	214.3	213.9
2	125.9	126.0	126.1	126.1	33.9	122.5	124.3	124.4	124.0	29.6	30.8
3	186.0	186.1	186.2	186.3	198.5	150.7	148.1	148.1	148.4	35.0	35.5
4	128.4	128.8	137.8	137.6	128.5	122.5	—	—	—	139.4	139.3
5	151.5	151.9	148.0	149.3	152.9	159.5	—	—	—	127.0	128.1
6	81.5	80.8	76.5	76.9	82.1	82.3	75.6	75.5	79.6	77.5	76.6
7	54.0	49.5	43.8	41.8	53.4	53.7	42.1	40.0	53.0	51.0	42.8
8	23.8	20.3	23.4	18.3	23.7	23.8	23.8	19.7	70.7	67.3	23.6
9	39.3	38.2	34.9	34.7	38.7	38.5	24.9	25.9	35.5	39.2	31.1
10	41.7	41.8	39.4	39.5	38.5	41.1	—	—	—	46.7	46.1
11	41.2	38.2	44.2	41.3	41.4	41.4	40.8	40.7	40.5	41.5	44.4
12	177.4	178.3	179.6	179.0	177.6	178.0	179.4	178.7	178.3	180.4	180.0
13	12.5	9.9	14.9	9.6	12.5	12.5	14.6	9.5	14.1	15.6	15.2
14	10.9	11.0	11.0	11.0	11.3	12.2	12.1	11.9	13.6	19.8	19.5
15	25.3	25.2	25.2	24.9	23.4	26.0	20.7	20.8	20.7	25.1	24.4

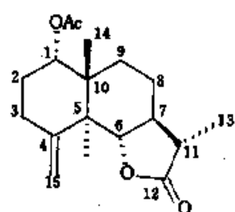


56　57　58　59　60

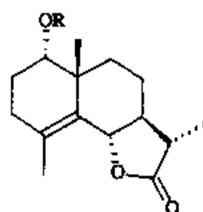
61　62. R = H　63. R = OAc　64　65. R = OH　66. R = H

表 21-11　桉烷型内酯 67～76 的^{13}C-NMR 谱化学位移数据[85]

化合物 / C	67	68	69	70	71	72	73	74	75	76
1	76.3	74.6	76.5	77.2	71.7	77.2	76.9	73.1	78.3	75.7
2	27.1	25.3	22.7	25.6	29.6	29.0	30.1	30.1	27.1	26.6
3	30.5	29.1	29.6	31.7	29.9	27.3	26.5	31.8	26.7	31.3
4	143.5	125.8	126.2	75.0	145.0	143.9	145.2	144.2	144.4	143.5
5	48.2	128.0	127.5	76.8	76.4	77.2	78.6	75.4	76.5	75.2
6	79.5	83.1	82.3	81.7	81.8	85.1	81.5	86.0	81.3	85.6
7	52.0	53.0	52.8	45.4	45.4	46.9	45.4	47.5	44.9	47.3
8	22.7	24.0	23.9	22.7	22.8	23.9	22.5	23.7	22.4	23.6
9	33.3	32.9	33.2	32.0	30.3	33.0	29.3	26.4	28.7	27.6
10	41.6	41.7	40.3	42.6	44.6	44.6	43.0	46.2	43.3	45.1
11	41.0	41.1	41.1	41.1	41.2	42.0	41.1	42.2	41.1	42.0
12	179.2	179.0	178.8	179.5	179.5	178.2	179.3	178.6	178.7	178.3
13	12.4	12.3	12.4	12.5	12.5	12.7	12.4	12.7	12.5	12.6
14	18.0	26.0	25.7	21.7	13.2	18.1	20.8	17.5	20.7	17.3
15	109.8	20.0	20.1	28.5	112.3	115.6	112.0	115.3	111.9	115.7
OAc	170.5		170.8						169.4	170.4
	21.2		21.3						21.2	21.2

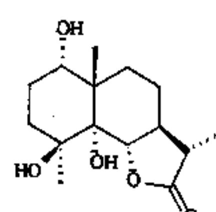


67

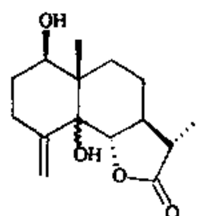


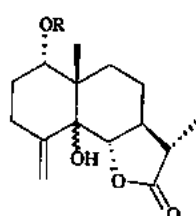
68. R = H

69. R = Ac



70





73. R = H, 5α-OH

74. R = H, 5β-OH

75. R = Ac, 5α-OH

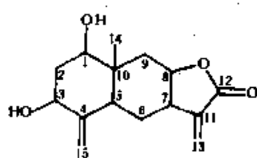
76. R = Ac, 5β-OH

71. 5α-OH

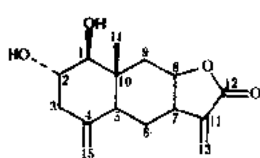
72. 5β-OH

表 21-12　桉烷型内酯 77 – 82 的^{13}C-NMR 化学位移数据[20]

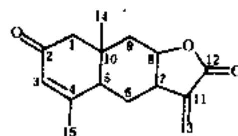
C \ 化合物	77	78	79	80	81	82
1	73.4	85.2	54.2	49.2	40.0	51.0
2	38.8	72.2	196.9	73.2	32.1	66.9
3	74.2	44.3	127.7	79.5	73.0	46.3
4	149.2	147.5	159.6	150.1	151.0	146.1
5	43.2	45.6	44.9	45.2	44.6	45.6
6	25.9	28.3	26.9	28.6	27.5	27.3
7	39.4	41.4	40.8	41.2	40.3	40.5
8	76.7	79.0	75.6	78.5	76.7	76.6
9	33.0	39.3	40.6	41.6	41.0	41.2
10	39.1	39.5	35.7	34.5	34.0	33.9
11	141.4	144.3	141.6	143.7	142.0	142.1
12	169.6	172.9	169.6	172.3	170.5	170.3
13	119.0	121.3	120.6	120.9	120.3	120.1
14	16.8	13.3	18.3	19.0	17.7	18.7
15	108.8	109.9	21.5	106.1	103.5	108.9

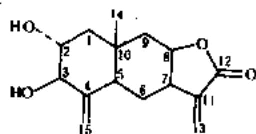


77

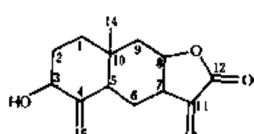


78

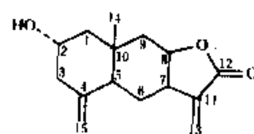

79



80



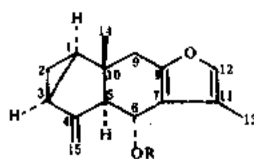
81



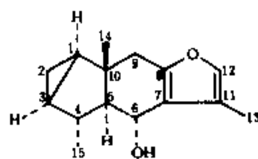
82

表 21-13　倍半萜内酯 83 ~ 90 的^{13}C-NMR 化学位移数据[21]

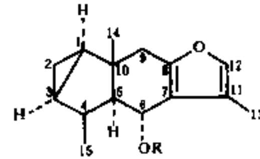
C \ 化合物	83	84	85	86	87	88	89	90
1	27.4	27.2	28.3	29.1	29.1	130.3 (2.5)	130.0 (1.6)	143.6
2	16.6	16.7	16.7	10.9	11.0	25.8 (2.8)	23.0 (1.8)	114.8
3	23.1	23.1	26.8	24.5	24.6	26.8 (4.5)	26.6 (2.9)	123.7
4	150.0	149.0	39.5	31.9	32.0	135.1 (2.6)	61.3 (6.2)	136.6
5	68.4	64.8	71.1	66.1	62.9	151.7 (4.9)	65.6 (4.6)	46.8
6	65.1	65.9	67.6	64.2	65.9	74.2 (4.2)	73.2 (2.7)	72.2
7	120.9	117.7	121.4	121.3	118.3	115.4 (2.3)	113.7 (1.2)	113.6
8	152.5	153.7	152.9	153.1	154.3	152.8 (2.2)	153.2 (1.1)	152.6
9	38.4	38.3	39.1	40.8	40.9	40.7 (1.8)	40.4 (0.9)	34.9
10	41.3	41.6	43.6	43.6	44.0	130.8 (4.0)	131.6 (1.4)	40.9
11	120.1	119.2	119.8	120.1	119.2	122.2 (1.3)	122.2 (0.6)	119.8
12	138.5	138.8	138.4	138.2	138.6	137.2 (1.0)	137.1 (0.4)	138.6
13	9.1	8.7	9.2	9.1	8.6	8.4 (0.4)	8.3 (0.2)	8.2
14	18.2	18.3	20.4	19.8	20.0	15.7 (2.9)	15.8 (1.4)	18.7
15	108.0	107.9	17.7	13.6	13.9	173.4 (8.7)	171.5 (5.0)	170.9
C=O	—	171.0	—	—	170.7	—	—	—
CH_3	—	21.1	—	—	21.0	—	—	—



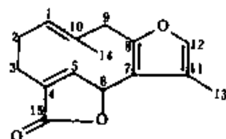
83. R = H
84. R = Ac



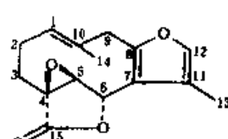
85



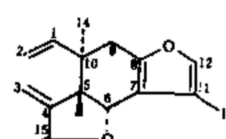
86. R = H
87. R = Ac



88



89

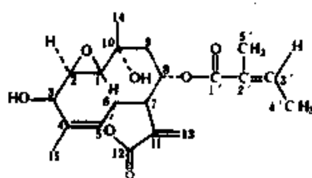


90

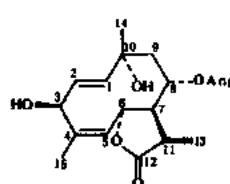
3. 吉马烷型倍半萜内酯的^{13}C-NMR 化学位移

表 21-14 吉马烷型内酯 91～96 的^{13}C-NMR 化学位移数据[22,23]

C \ 化合物	91	92	93	94	95	96	C \ 化合物	91	92	93	94	95	96
1	60.0	131.9	38.9	128.8	128.8	128.5	11	134.9	135.5	137.2	127.0	121.3	126.7
2	56.9	130.5	38.4	31.8	32.0	35.6	12	167.3	168.0	169.4	169.0	168.5	168.5
3	69.9	72.9	108.8	23.9	23.9	23.9	13	122.9	122.6	121.4	122.8	122.7	122.3
4	143.8	146.8	43.4	64.5	64.4	61.8	14	27.8	29.5	26.9	12.8	12.9	12.4
5	126.8	125.9	38.0	66.8	67.0	66.2	15	25.4	25.1	—	60.8	60.8	16.9
6	74.4	73.9	81.3	75.0	74.8	75.6	1′	169.3	169.4	176.1	166.2	165.7	165.9
7	51.2	51.3	47.9	79.8	49.8	41.4	2′	127.1	127.1	34.1	136.4	136.3	136.0
8	67.1	68.9	69.8	74.0	74.2	74.0	3′	140.1	140.7	—	142.9	137.3	142.6
9	41.3	43.8	42.4	44.0	44.1	43.5	4′	20.5	20.4	—	59.6	61.2	59.1
10	67.4	70.8	80.0	132.2	132.1	131.2	5′	15.9	15.9	—	19.6	19.9	11.4

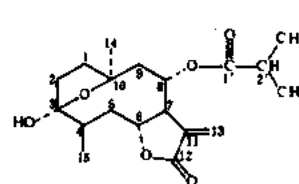


91

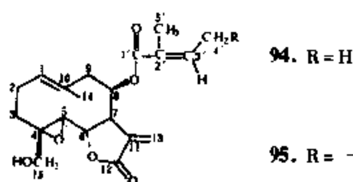


92

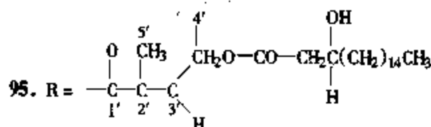
Ang = 当归酰基



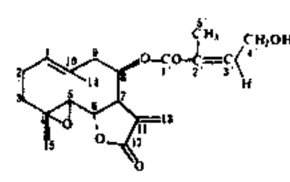
93



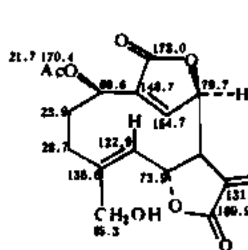
94. R = H



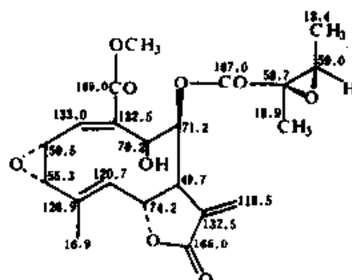
95. R = $-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=\overset{H}{C}-CH_2O-CO-CH_2C(OH)(H)(CH_2)_{14}CH_3$



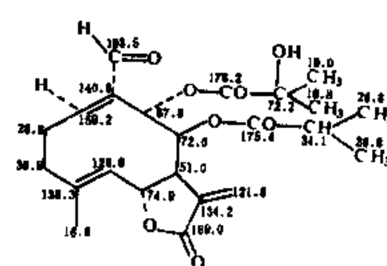
96



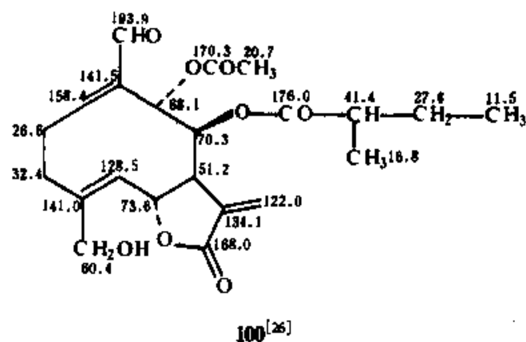
97[24]



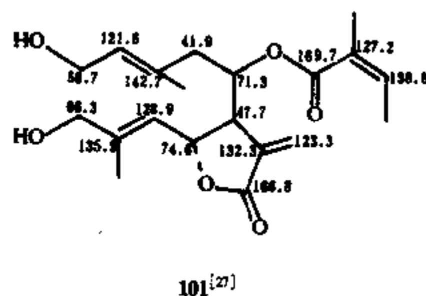
98[25]



99[26]



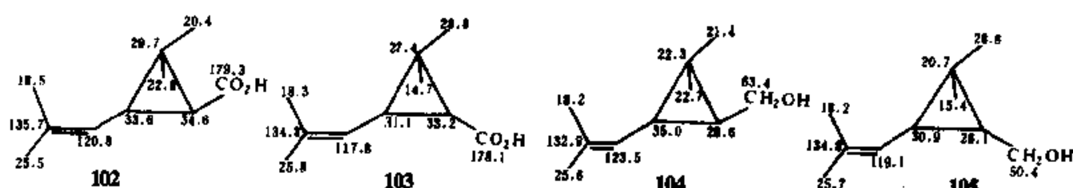
100[26]



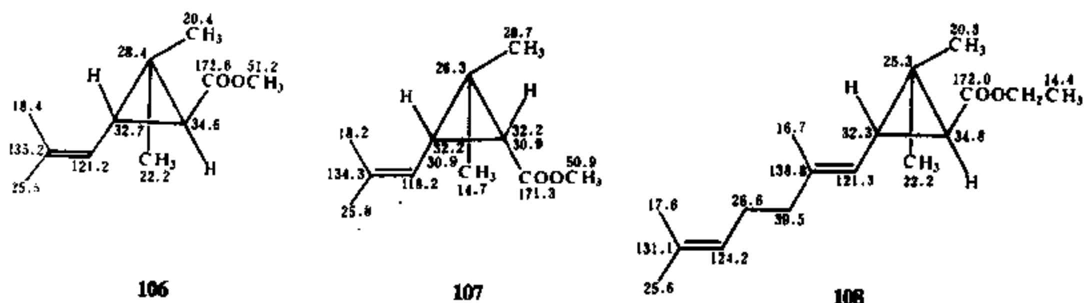
101[27]

CH₃: 20.3, 15.8, 15.6, 14.0

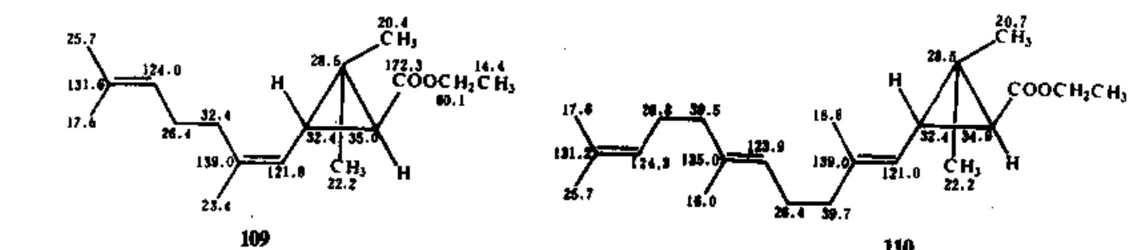
三、几个三元环萜的^{13}C-NMR 化学位移[28]



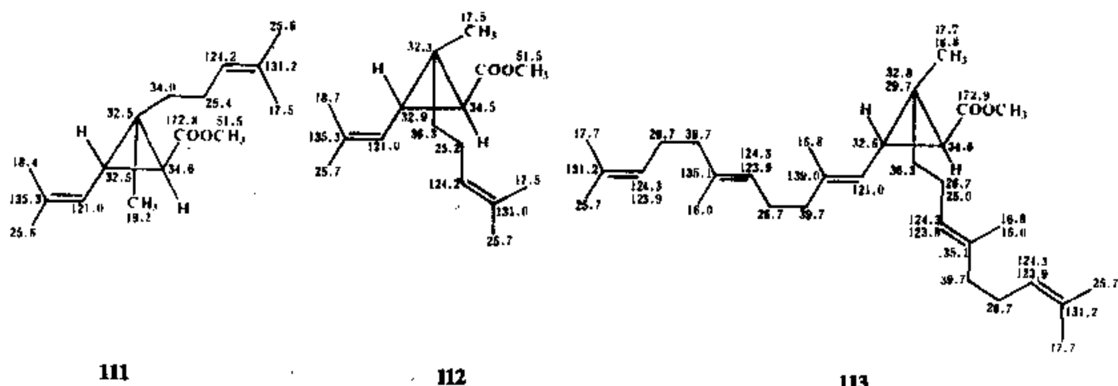
102　103　104　105



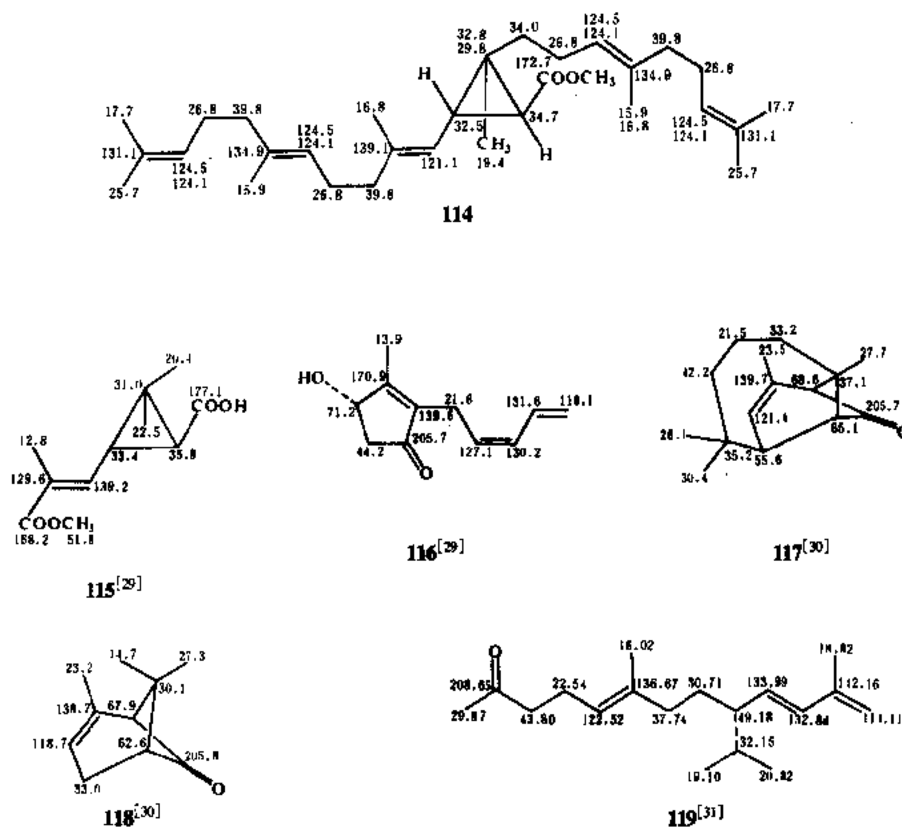
106　107　108



109　110



111　112　113



四、特殊倍半萜内酯的^{13}C-NMR 化学位移

表 21-15　倍半萜内酯 120～126 的^{13}C-NMR 化学位移数据[32]

C \ 化合物	120	121	122	123	124	125	126
1	43.0	79.4	78.3	133.3	134.3	61.5	62.0
2	22.6	24.4	22.5	25.2	25.7	140.3	146.9
3	31.6	27.5	29.1	34.8	34.3	127.3	123.6
4	168.8	177.1	176.5	170.9	173.9	160.3	160.0
5	89.8	93.6	91.7	80.7	86.5	85.8	85.6
6	86.2	83.4	82.3	83.5	85.9	81.2	82.0
7	41.3	41.6	41.4	41.5	41.9	39.2	41.7
8	30.9	30.2	29.3	30.0	35.0	31.1	32.0
9	24.0	26.9	26.7	26.0	25.7	25.6	22.8
10	35.3	40.1	40.6	126.1	132.4	66.8	71.0
11	138.3	138.8	138.5	138.5	138.8	138.9	137.6
12	169.4	169.5	169.3	169.8	170.2	169.1	169.0
13	120.2	121.6	121.3	120.6	120.1	121.9	121.1
14	18.9	21.6	21.4	23.7	24.7	24.2	20.9
15	14.4	15.1	15.0	23.1	22.8	21.0	21.9
—CH_2—	—	—	—	—	60.2	—	—
—CH_3	—	—	—	—	14.3	—	—

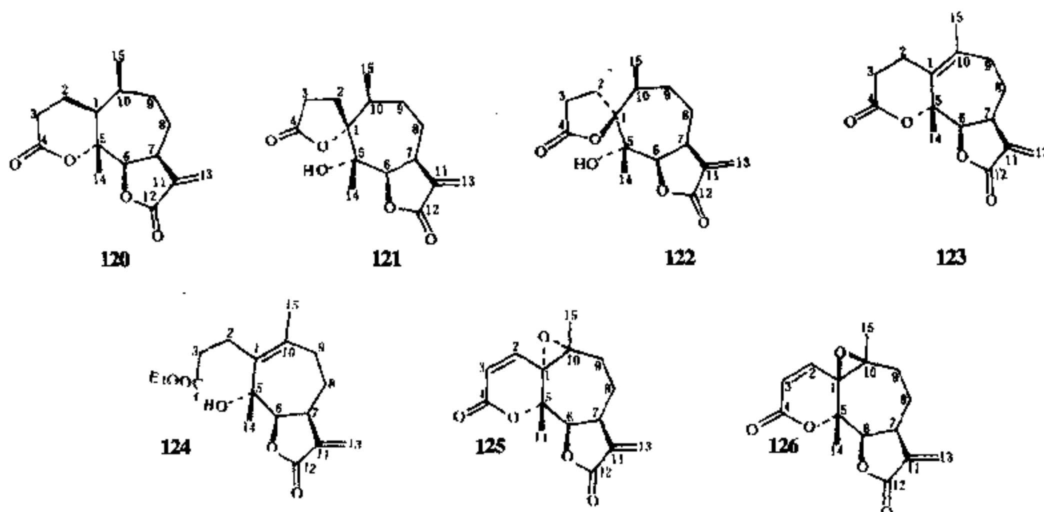
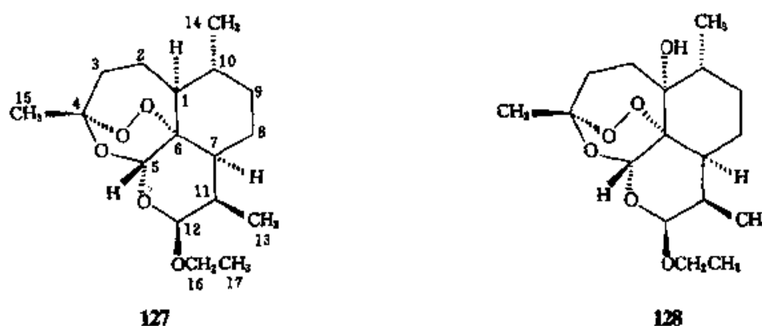


表 21-16　两个倍半萜过氧化物的^{13}C-NMR 化学位移数据[86]

C \ 化合物	127	128	C \ 化合物	127	128	C \ 化合物	127	128
1	52.8	76.0	7	44.7	39.9	13	13.1	13.0
2	24.8	28.8	8	24.6	23.8	14	20.4	15.3
3	36.6	33.8	9	34.8	33.3	15	26.3	26.0
4	104.0	103.7	10	37.6	40.7	16	63.8	63.9
5	87.9	87.2	11	31.0	31.0	17	15.3	15.2
6	81.2	82.3	12	101.7	102.1			



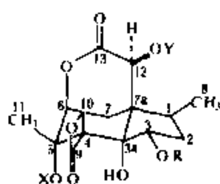
五、五、六元环倍半萜的^{13}C-NMR 化学位移

1. 五元、六元环倍半萜的^{13}C-NMR 化学位移

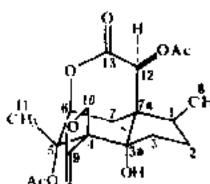
表 21-17　五、六元环倍半萜 129～136 的^{13}C-NMR 化学位移数据[33]①

C \ 化合物	129	130	131	132	133	134	135	136
1	36.7 (d)	36.6 (d)	36.2 (d)	37.2 (d)	31.2 (d)	30.2 (d)	33.3 (d)	36.0 (d)
2	37.3 (t)	37.4 (t)	37.3 (t)	30.1 (t)	34.8 (t)	43.9 (t)	28.7 (t)	37.3 (t)
3	73.4 (d)	74.4 (d)	73.7 (d)	33.3 (t)	73.2 (d)	204.6 (s)	32.5 (t)	74.5 (d)
3a	84.6 (s)	82.4 (s)	82.3 (s)	83.3 (s)	79.4 (s)	72.5 (s)	80.4 (s)	86.7 (s)
4	64.0 (s)	65.0 (s)	64.8 (s)	66.0 (s)	66.6 (s)	64.2 (s)	67.9 (s)	57.6 (s)
5	74.3 (s)	82.4 (s)	82.3 (s)	83.1 (s)	79.7 (s)	83.2 (s)	81.4 (s)	83.4 (s)
6	81.5 (d)	76.3 (d)	75.5 (d)	75.4 (d)	79.0 (d)	81.5 (d)	78.6 (d)	77.4 (d)
7	26.3 (t)	26.5 (t)	26.7 (t)	27.3 (t)	29.4 (t)	29.5 (t)	29.7 (t)	28.9 (t)
7a	49.4 (s)	49.2 (s)	49.7 (s)	50.2 (s)	56.9 (s)	57.8 (s)	59.2 (s)	55.2 (s)
8	13.3 (q)	13.4 (q)	13.2 (q)	13.2 (q)	13.4 (q)	12.0 (q)	12.8 (q)	12.4 (q)
9	167.8 (s)	166.8 (s)	166.3 (s)	165.9 (s)	166.4 (s)	166.1 (s)	166.5 (s)	170.7 (s)
10	64.7 (t)	64.2 (t)	64.3 (t)	64.8 (t)	65.9 (t)	66.6 (t)	66.5 (t)	41.5 (t)
11	20.7 (q)	17.7 (q)	17.6 (q)	17.8 (q)	19.2 (q)	20.6 (q)	19.3 (q)	19.0 (q)
12	69.7 (d)	69.6 (d)	68.4 (d)	68.8 (d)				76.7 (s)
13	174.0 (s)	174.2 (s)	167.4 (s)	166.6 (s)	174.1 (s)	172.2 (s)	174.7 (s)	176.8 (s)
$COOCH_3$								52.4 (s)

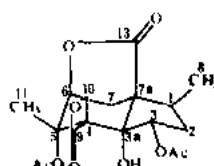
① 括号内表示峰型：s—单峰；d—双峰；t—三重峰；q—四重峰。



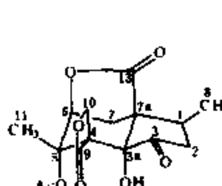
129. R = Ac, X = Y = H
130. R = X = Ac, Y = H
131. R = X = Y = Ac



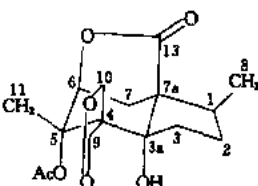
132



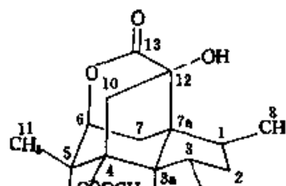
133



134



135

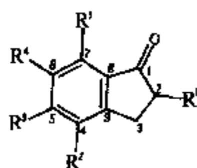


136

2. 茚满酮类倍半萜的^{13}C-NMR 化学位移

表 21-18 茚满酮类倍半萜 137～147 的^{13}C-NMR 化学位移数据[34]

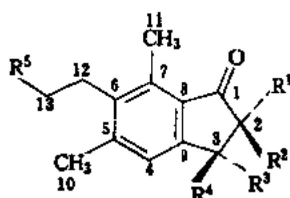
C \ 化合物	137	138	139	140	141	142	143	144	145	146	147
1	206.1	209.2	206.3	207.7	208.7	209.0	210.1	210.5	208.8	209.2	210.5
2	36.0	42.0	36.3	36.8	42.1	42.2	42.3	42.1	42.2	42.4	42.7
3	25.7	35.0	25.6	25.4	34.8	34.6	34.6	33.5	34.6	34.4	34.0
4	126.6	126.5	127.0	124.0	126.9	126.2	123.8	132.6	127.3	124.1	123.3
5	134.3	134.6	145.6	133.9	145.7	135.8	133.9	134.4	144.3	144.8	135.7
6	127.0	127.4	128.5	129.1	128.6	137.2	129.2	129.3	136.2	130.3	136.1
7	123.2	124.0	123.4	138.9	123.8	123.8	139.0	136.1	124.3	138.5	137.3
8	136.9	136.4	134.8	134.5	134.1	135.8	133.8	133.5	134.5	131.5	133.6
9	155.0	153.4	155.6	155.9	153.9	150.7	154.1	152.9	151.5	154.4	151.8
C_2—CH_3		16.4			16.4	16.3	16.4	16.5	16.4	16.4	16.4
C_4—CH_3								17.4			
C_5—CH_3			22.0		22.0				20.6	21.7	
C_6—CH_3						21.0			19.6		18.9
C_7—CH_3				18.2			18.2	17.8		18.0	13.5



化合物	R¹	R²	R³	R⁴	R⁵	化合物	R¹	R²	R³	R⁴	R⁵
137	H	H	H	H	H	143	CH_3	H	H	H	CH_3
138	CH_3	H	H	H	H	144	CH_3	CH_3	H	H	CH_3
139	H	H	CH_3	H	H	145	CH_3	H	CH_3	CH_3	H
140	H	H	H	H	CH_3	146	CH_3	H	CH_3	H	CH_3
141	CH_3	H	CH_3	H	H	147	CH_3	H	H	CH_3	CH_3
142	CH_3	H	H	CH_3	H						

表 21-19　茚满酮类倍半萜 148 ~ 158 的^{13}C-NMR 化学位移数据[34]

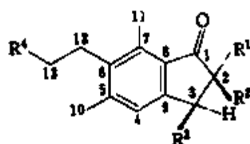
C \ 化合物	148	149	150	151	152	153	154	155	156	157	158
1	212.4	212.7	208.2	210.5	211.6	210.0	209.8	211.7	209.8		212.3
2	43.7	52.6	55.5	50.4	52.4	42.5	49.9	50.6	56.9	77.5	45.6
3	34.7	37.5	76.9	71.2	77.5	33.8	29.7	36.9	77.6	41.1	41.7
4	126.8	126.8	126.4	127.3	126.1	125.9	126.9	126.0	125.9	125.4	125.8
5	146.0	146.0	146.9	146.9	146.3	143.8	146.1	144.5	146.4	145.6	144.4
6	136.3	136.2	138.8	138.8	138.2	134.5	136.3	134.8	138.0	135.4	134.8
7	138.6	138.6	136.9	139.3	138.3	137.7	138.5	138.1	138.3	138.7	138.3
8	132.8	133.1	131.1	131.1	131.4	132.2	133.9	131.7	132.7		131.0
9	154.2	153.8	152.8	153.4	153.7	153.0	155.2	152.7	154.7	149.9	151.3
10	21.3	21.4	21.1	21.1	21.4	21.1	21.4	21.2	21.5	21.4	21.3
11	13.8	13.9	14.9	15.7	14.1	13.6	13.9	13.7	14.2	14.1	13.7
12	32.9	32.9	33.9	33.9	33.1	32.2	32.9	32.2	33.1	31.8	31.9
13	61.6	61.6	62.9	62.9	61.6	42.0	61.7	42.0	11.6	61.5	61.5
R^1	16.8	68.2	14.9	12.1	23.5	16.5	63.1	68.0	67.1	26.1	25.5
R^2		21.3			20.8			21.0	19.2		25.5

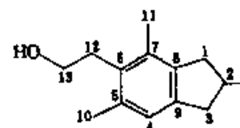


化合物	R^1	R^2	R^3	R^4	R^5	化合物	R^1	R^2	R^3	R^4	R^5
148	CH_3	H	H	H	OH	154	CH_2OH	H	H	H	OH
149	CH_2OH	CH_3	H	H	OH	155	CH_2OH	CH_3	H	H	Cl
150	H	CH_3	OH	H	OH	156	CH_2OH	CH_3	OH	H	OH
151	CH_3	H	OH	H	OH	157	CH_3	OH	H	H	OH
152	CH_3	CH_3	OH	H	OH	158	CH_3	CH_3	H	H	OH
153	CH_3	H	H	H	Cl						

表 21-20　茚满酮类倍半萜 159 ~ 165 的^{13}C-NMR 化学位移数据[34]

C \ 化合物	159	160	161	162	163	164	165
1	210.6	210.0	210.4	209.6	205.8	208.6	40.6
2	42.6	42.7	51.3	42.5	53.0	47.6	33.9
3	33.9	34.0	36.3	33.7	74.2	68.5	41.4
4	125.8	125.9	126.0	126.1	124.0	125.0	124.0
5	144.2	144.3	144.4	144.5	144.7	144.7	134.9
6	134.0	134.2	134.9	135.2	136.2	136.2	132.0
7	138.0	138.1	136.9	137.2	136.3	136.6	132.7
8	132.2	132.3	131.8	131.8	130.7	130.5	141.0
9	152.7	157.8	152.5	152.7	153.0	153.6	141.5
10	21.1	21.2	21.0	21.3	19.9	19.9	20.4
11	13.6	13.7	13.3	13.6	12.4	12.5	16.2
12	28.0	28.2	29.1	29.4	28.6	28.6	32.9
13	62.8	62.7	66.9	67.3	67.1	67.1	62.1
R^1	16.6	16.7	66.8	16.7	16.7		21.2
R^2			21.0			11.6	
1′	170.9	173.8	102.8	103.1	102.4	102.4	
2′	20.9	32.0	70.1	73.8	73.1	73.1	
3′		29.8	76.8	77.0	75.9	75.9	
4′		29.6	70.1	70.4	69.6	69.6	
5′		29.5	76.8	77.0	76.2	76.2	
6′		29.4	61.4	61.7	61.1	61.1	
7′		29.3					
8′		25.0					
9′		22.7					
10′		14.2					





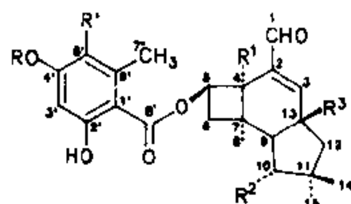
165

159. $R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = OAc$
160. $R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = O$-棕榈酰基
161. $R^1 = CH_2OH$, $R^2 = CH_3$, $R^3 = H$, $R^4 = O$-Glu
162. $R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = O$-Glu
163. $R^1 = CH_3$, $R^2 = H$, $R^3 = OH$, $R^4 = O$-Glu
164. $R^1 = H$, $R^2 = CH_3$, $R^3 = OH$, $R^4 = O$-Glu

3. 原伊鲁烷类倍半萜的^{13}C-NMR 化学位移

表 21-21　原伊鲁烷类倍半萜 166 ~ 176 的^{13}C-NMR 的化学位移数据[34a]

C \ 化合物	166	167	168	169	170	171	172	173	174	175	176
1	195.6	195.6	196.0	195.6	195.7	196.2	196.3	196.1	195.8	194.1	194.4
2	137.8	137.4	137.7	135.6	135.4	136.8	136.7	137.0	134.8	138.3	138.0
3	157.8	157.8	158.2	158.4	158.8	153.0	153.1	152.7	152.5	151.4	157.1
4	75.3	74.9	75.6	74.4	74.3	77.8	77.8	77.9	77.4	40.3	39.6
5	77.6	77.8	77.6	75.6	76.1	74.6	75.2	74.7	73.7	66.7	69.7
6	33.4	33.1	33.1	32.8	32.8	31.6	31.6	31.7	32.1	37.0	39.5
7	38.1	37.8	38.2	35.3	35.5	37.5	37.5	37.5	35.6	32.1	32.2
8	21.4	21.0	21.3	20.8	20.8	21.4	21.4	21.4	20.8	26.9	26.5
9	44.4	44.1	44.5	47.4	47.4	50.3	50.2	50.4	54.9	50.2	45.4
10	41.8	41.6	41.5	80.5	80.5	43.2	43.2	43.3	81.5	43.3	42.0
11	37.6	37.6	37.9	42.7	42.7	34.6	34.6	34.6	41.2	33.7	37.8
12	46.6	46.6	46.8	43.2	43.1	58.1	58.1	58.2	55.2	58.2	47.0
13	40.4	40.2	40.8	36.1	36.1	75.4	75.2	75.4	77.2	78.3	40.7
14	31.6	31.4	31.6	28.3	28.3	30.8	30.9	30.9	28.2	31.5	31.7
15	31.1	30.9	31.2	23.3	23.3	30.8	30.8	30.3	23.2	31.2	31.5
1′	105.0	106.4	105.3	104.9	106.3	105.0	106.3	105.4	104.9	105.1	105.3
2′	165.7	162.8	165.8	165.8	163.0	165.7	162.9	165.5	165.8	165.6	165.6
3′	99.0	98.5	101.5	98.8	98.6	98.8	98.6	101.5	98.8	98.8	101.4
4′	163.9	159.3	160.5	164.0	159.7	164.0	159.5	160.2	164.1	163.8	160.4
5′	111.1	115.2	111.5	111.2	115.4	111.2	115.4	111.2	111.2	111.1	111.1
6′	142.5	138.7	144.1	142.5	139.1	142.7	139.1	143.5	142.6	142.7	143.4
7′	24.5	19.5	24.6	24.5	19.8	24.6	19.8	24.5	24.5	24.6	24.4
8′	170.8	170.1	170.5	170.7	170.2	170.9	170.2	170.0	170.7	170.6	170.6
OCH_3	55.2	56.0	—	55.3	56.3	55.3	56.3	—	55.3	55.3	—

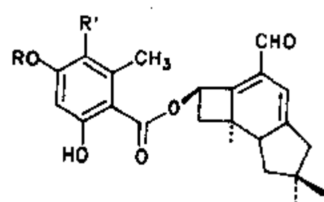


166. R = CH_3, R' = R^2 = R^3 = H, R^1 = OH
167. R = CH_3, R' = Cl, R^1 = OH, R^2 = R^3 = H
168. R = R' = R^2 = R^3 = H, R^1 = OH
169. R = CH_3, R' = R^3 = H, R^1 = R^2 = OH
170. R = CH_3, R' = Cl, R^1 = R^2 = OH, R^3 = H
171. R = CH_3, R' = R^2 = H, R^1 = R^3 = OH
172. R = CH_3, R' = Cl, R^1 = R^3 = OH, R^2 = H
173. R = R' = R^2 = H, R^1 = R^3 = OH
174. R = CH_3, R' = H, R^1 = R^2 = R^3 = OH
175. R = CH_3, R' = R^1 = R^2 = H, R^3 = OH
176. R = R' = R^1 = R^2 = R^3 = H

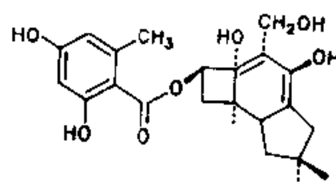
表 21-22 原伊鲁烷类倍半萜 177～182 的 ^{13}C-NMR 的化学位移数据[34a]

化合物 / C	177	178	179①	180①	181	182	化合物 / C	177	178	179①	180①	181	182
1	187.5	187.6	62.9	171.0	—	—	13	150.3	150.2	47.7	40.9	38.4	38.7
2	129.4	129.8	46.5	128.5	136.3	135.4	14	29.4	30.0	32.8	32.1	31.8	31.8
3	110.3	111.0	69.6	148.4	121.3	124.3	15	29.3	29.6	32.4	31.6	31.5	31.6
4	160.6	160.3	82.2	76.5	78.7	73.6	1'	105.9	105.3	105.9	105.4	105.7	105.1
5	72.3	72.0	76.4	78.0	75.7	79.1	2'	163.5	165.6	166.2	166.7	165.4	165.6
6	39.4	39.2	34.6	33.8	35.4	32.3	3'	98.6	98.8	101.8	101.7	101.2	101.4
7	36.3	36.5	39.3	38.8	38.0	38.0	4'	160.1	163.9	163.8	163.8	160.4	160.7
8	27.4	27.0	22.3	22.2	22.2	21.7	5'	115.2	111.2	112.5	112.5	111.1	111.5
9	45.7	45.5	48.6	45.0	43.7	44.0	6'	139.5	142.5	144.4	144.9	144.5	144.4
10	40.9	40.8	44.8	42.8	41.8	41.7	7'	20.1	24.5	24.4	24.6	24.5	24.4
11	37.4	37.3	37.1	38.9	37.3	37.7	8'	170.2	170.1	172.6	172.2	169.9	172.1
12	48.6	48.5	43.9	47.8	47.6	47.4	OCH_3	56.3	55.3	—	—	—	—

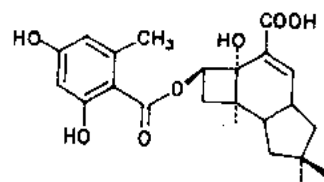
① 在 CD_3OD 中测定。



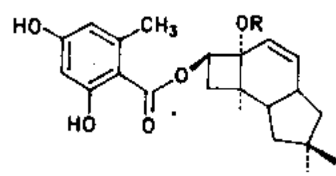
177. R = CH_3, R' = H
178. R = CH_3, R' = Cl



179



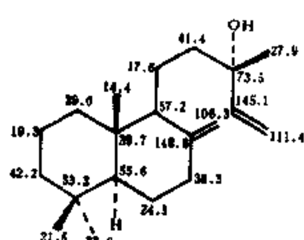
180



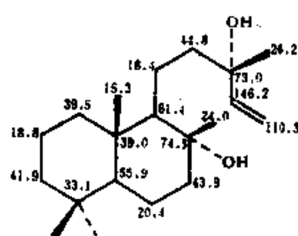
181. R = CO $(CH_2)_{14}CH_3$
182. R = H

第四节　二萜化合物的13C-NMR化学位移

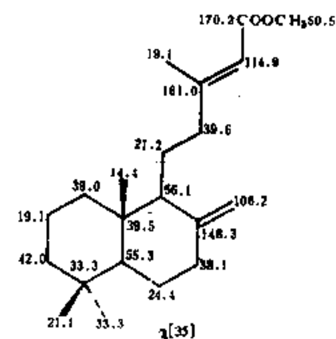
一、二萜醇、二萜醚和二萜内酯的13C-NMR化学位移



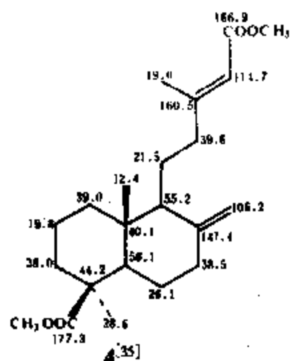
1[35]



2[35]

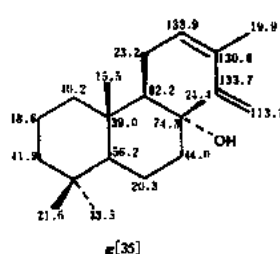


3[35]

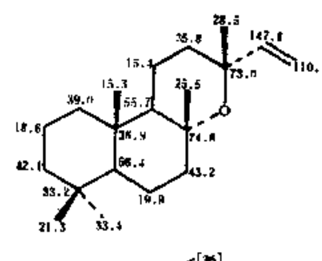


4[35]

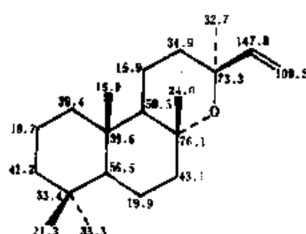
OMe：50.9，50.5



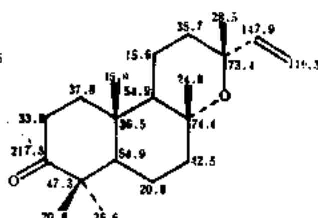
5[35]



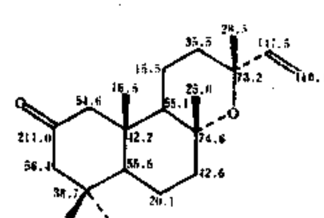
6[36]



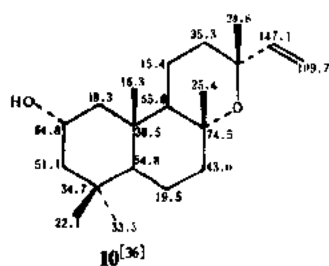
7[36]



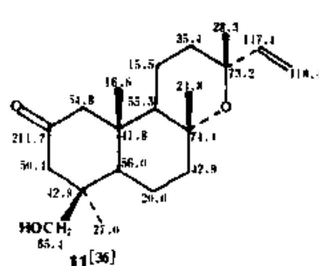
8[36]



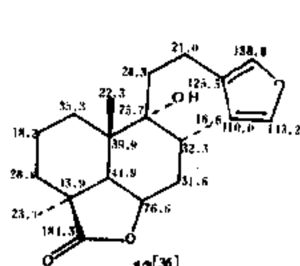
9[36]



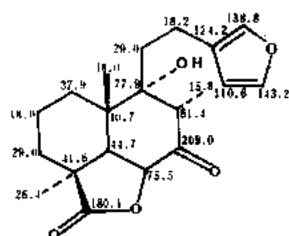
10[36]



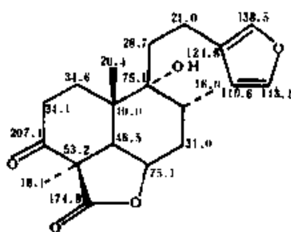
11[36]



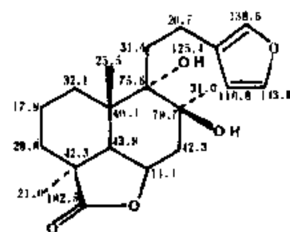
12[36]



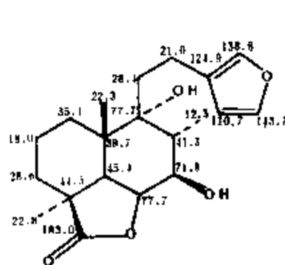
13[37]



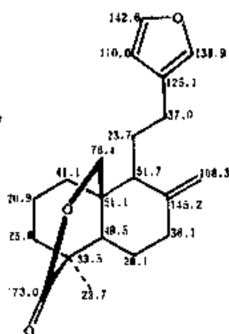
14[37]



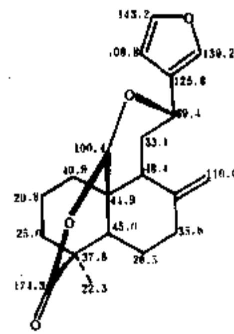
15[37]



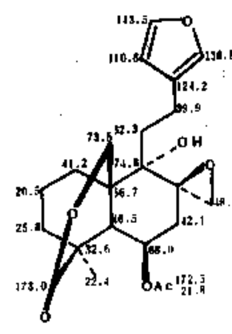
16[37]



17[38]



18[38]

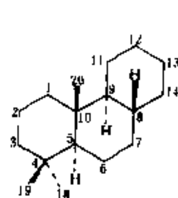


19[38]

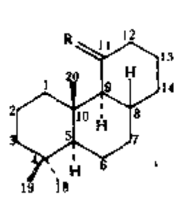
二、三环二萜化合物的^{13}C-NMR 化学位移

表 21-23　三环二萜化合物 20 ~ 31 的^{13}C-NMR 化学位移数据[39]

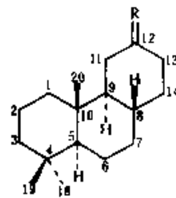
C \ 化合物	20	21	22	23	24	25	26	27	28	29	30	31
1	39.1	41.7	39.6	38.8	39.0	39.3	39.4	38.9	39.0	38.4	38.7	39.4
2	19.0	19.1	18.7	18.9	18.9	18.9	19.0	18.8	18.8	18.7	18.7	19.0
3	42.4	42.0	42.2	42.2	42.2	42.2	42.2	42.2	42.1	42.3	42.0	42.0
4	33.3	33.6	33.2	33.3	33.2	33.3	33.2	33.3	33.2	33.3	33.2	33.3
5	55.5	55.3	55.7	55.4	55.2	54.9	55.1	55.4	55.1	54.9	54.8	54.6
6	21.8	21.9	21.7	21.7	21.6	21.5	21.1	21.6	21.6	21.2	21.4	20.6
7	35.9	35.7	36.0	35.4	34.9	30.6	31.0	35.3	34.7	35.8	34.3	26.3
8	36.8	36.4	30.1	36.4	35.6	40.7	44.1	36.1	35.7	40.0	35.6	49.7
9	56.3	62.0	58.9	48.5	53.9	48.2	53.9	49.4	53.6	67.4	56.1	75.3
10	36.9	39.0	37.5	36.4	36.7	36.7	36.7	36.4	36.8	36.7	37.3	37.6
11	25.1	71.9	66.4	31.5	34.6	24.8	24.4	29.2	30.9	211.8	41.0	24.4
12	27.1	38.4	35.4	67.0	71.4	20.0	24.0	70.7	74.4	44.3	213.4	26.5
13	26.4	23.9	19.1	32.3	35.2	33.6	35.4	29.0	31.5	26.7	41.1	41.8
14	35.5	34.9	35.6	28.6	32.9	71.0	76.8	28.8	32.4	34.5	34.2	213.7
18	33.6	33.9	34.0	33.6	33.6	33.6	33.6	33.6	33.6	33.7	33.6	33.5
19	22.0	22.1	22.1	21.7	21.9	22.0	21.9	21.9	21.9	22.0	21.9	21.9
20	14.3	15.0	16.7	14.1	14.3	14.1	14.3	14.0	14.2	14.6	13.8	13.9



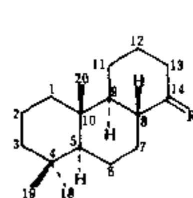
20



21. R = H, α-OH
22. R = H, β-OH
29. R = O



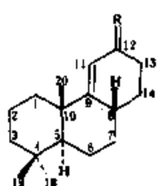
23. R = H, α-OH
24. R = H, β-OAc
27. R = H, α-OAC
28. R = H, β-OAc
30. R = O



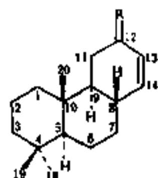
25. R = H, α-OH
26. R = H, β-OH
31. R = O

表 21-24　三环二萜化合物 32～42 的^{13}C-NMR 化学位移数据[39]

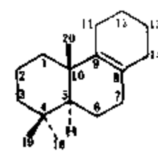
C \ 化合物	32	33	34	35	36	37	38	39	40	41	42
1	37.6	37.3	37.4	37.3	37.3	36.7	38.4	38.4	38.4	38.0	36.5
2	19.2	19.0	19.0	19.0	19.0	18.7	18.8	18.8	18.8	18.6	19.0
3	42.5	42.3	42.3	42.2	42.2	41.7	42.3	42.3	42.2	42.0	42.0
4	33.8	33.8	33.7	33.8	33.8	33.9	33.3	33.3	33.3	33.2	33.3
5	54.0	53.5	53.8	53.3	53.8	53.1	55.7	55.4	55.3	54.8	51.9
6	21.2	22.0	21.9	21.9	21.9	21.4	21.9	21.9	21.9	21.7	19.1
7	36.4	35.7	36.2	35.5	35.9	35.2	33.7	33.9	33.8	32.9	32.6
8	33.4	33.3	33.4	33.4	33.3	34.2	36.5	36.3	36.2	36.6	138.4
9	151.5	155.2	153.1	157.4	155.7	175.9	47.4	52.6	52.3	54.0	125.9
10	39.6	39.6	39.3	39.8	39.7	40.9	36.2	36.4	36.5	36.6	37.8
11	114.3	117.4	119.3	113.4	114.8	119.5	30.6	32.3	28.1	37.8	23.0
12	26.0	66.2	67.4	69.5	70.8	200.4	65.0	69.6	72.5	201.1	23.9
13	22.2	29.2	31.1	26.8	27.0	35.8	126.7	129.9	125.6	128.1	23.6
14	32.0	26.6	28.6	26.6	27.9	29.4	137.8	135.0	137.0	155.9	30.8
18	33.4	33.3	33.3	33.3	33.3	33.3	33.5	33.4	33.4	33.4	33.3
19	21.9	21.9	21.9	21.9	21.9	22.0	21.7	21.6	21.6	21.7	21.7
20	21.1	21.0	19.0	21.1	20.9	21.1	14.6	14.3	14.2	14.4	19.3



32. R = H_2
33. R = H, α-OH
34. R = H, β-OH
35. R = H, α-OAc
36. R = H, β-OAc
37. R = O



38. R = H, α-OH
39. R = H, β-OH
40. R = H, β-OAc
41. R = O



42

表 21-25　二萜化合物 43～50 的^{13}C-NMR 谱化学位移数据[87,88]

C \ 化合物	43	44	45	46	47	48	49	50
1	36.5	37.1	32.9	32.4	32.1	33.6	30.9	38.0
2	28.1	28.2	19.0	18.6	17.0	17.6	17.6	17.9
3	80.6	78.9	42.5	41.9	36.8	37.5	36.7	37.0
4	37.8	39.1	33.2	33.2	47.1	47.5	46.8	46.4
5	49.9	50.0	48.3	46.1	49.2	40.5	38.2	44.9
6	18.7	19.0	22.1	30.6	21.7	20.6	19.9	25.8
7	30.5	30.7	30.4	73.7	36.8	27.5	25.0	125.2
8	134.4	134.7	37.7	45.1	77.0	144.0	144.3	134.0
9	146.3	146.8	52.7	53.0	50.1	82.2	80.8	44.2
10	37.1	37.4	38.8	38.5	36.3	38.7	39.2	33.9
11	124.2	124.3	44.8	44.6	25.0	23.6	21.8	27.7
12	123.9	123.9	44.3	44.1	74.7	25.3	24.3	68.6
13	145.7	145.7	76.5	76.2	149.1	79.8	79.2	139.5
14	126.7	126.7	38.5	34.3	124.6	127.0	127.0	128.2
15	33.4	33.5	30.9	31.8	31.1	32.3	32.2	32.5
16	23.9	23.9	24.3	25.9	20.2	17.5	17.5	16.8
17	23.9	23.9	23.1	23.1	20.4	17.2	17.1	17.9
18	28.1	28.2	22.2	21.9	178.9	179.0	178.5	178.7
19	16.5	15.3	33.8	33.4	16.6	17.7	17.9	21.4
20	24.9	24.8	17.5	17.5	15.2	18.1	19.2	14.1
OMe					52.1	52.1	52.0	51.8
OCO								170.9
—Me								21.7

43. R = Ac

44. R = H

45

46

47

48

49

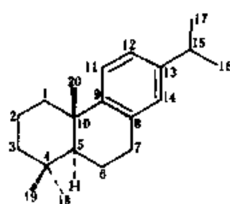
50

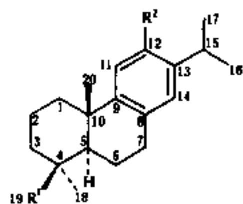


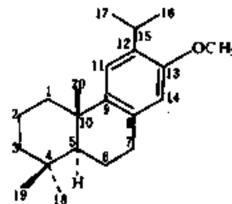
三、含芳香环的三环二萜的^{13}C-NMR 化学位移

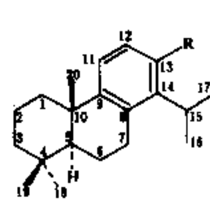
表 21-26　含芳香环的三环二萜 51～61 的^{13}C-NMR 化学位移数据[40]

化合物 / C	51	52	53	54	55	56	57	58	59	60	61









51. R = CH_3
52. R = CH_2OH
53. R = CHO
54. R = $COOCH_3$

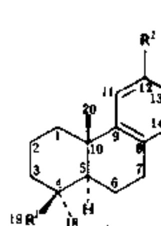
55. $R^1 = CH_3$，$R^2 = OCOCH^3$
56. $R^1 = CH_2OH$，$R^2 = OCH_3$
57. R^1 = CHO，$R^2 = OCH_3$
58. $R^1 = COOCH_3$，$R^2 = OCH_3$

59

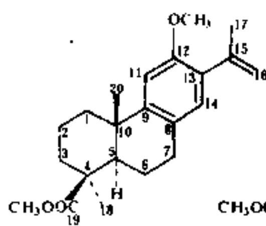
60. R = OH
61. R = $OCOCH_3$

表 21-27 含芳香环的三环二萜 62～70 的^{13}C-NMR 化学位移数据[40]

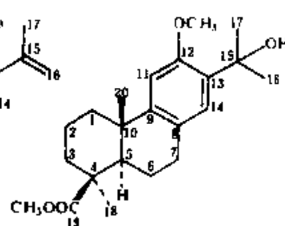
C \ 化合物	62	63	64	65	66	67	68	69	70
1	38.7	38.9	38.9	38.4	39.4	39.4	39.5	39.5	39.6
2	19.3	19.3	19.0	19.0	20.0	20.0	20.0	20.0	20.1
3	41.7	41.7	35.1	33.9	37.6	37.7	37.7	37.7	37.7
4	33.4	33.5	38.7	48.6	44.0	44.0	44.0	44.0	44.0
5	50.2	50.3	51.2	51.9	52.8	52.9	52.9	52.8	52.4
6	19.1	19.2	19.2	19.2	21.1	21.0	21.2	21.2	20.4
7	29.6	29.6	30.1	30.4	31.2	32.1	31.2	31.4	25.8
8	127.5	127.5	127.1	126.8	127.6	135.4	130.4	127.4	124.6
9	151.7	151.4	151.0	148.4	149.3	148.1	148.0	147.5	149.5
10	37.9	38.0	37.9	38.3	38.6	38.5	38.7	38.5	38.5
11	112.7	110.1	110.2	111.3	111.2	125.4	108.2	108.3	177.7
12	153.2	157.7	157.7	157.9	157.8	125.8	155.0	155.1	126.1
13	111.1	110.7	110.9	110.7	111.2	125.6	127.3	133.5	106.4
14	130.0	129.7	129.8	129.9	129.8	129.1	129.7	126.3	157.0
15							143.9	72.2	
16							114.7	29.9	
17							23.3	29.8	
18	33.3	33.3	26.8	24.2	28.5	28.5	28.5	28.5	28.5
19	21.6	21.7	65.1	205.6	177.8	177.9	177.9	177.7	177.9
20	24.7	24.7	25.6	24.1	22.9	23.0	22.9	22.8	22.7
OCH_3		55.2	55.2	55.2	55.1		55.7	55.3	
OCH_3					51.2	51.2	51.2	51.1	51.2



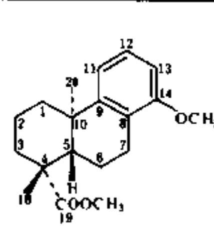
62. $R^1 = CH_3$，R^2 = OH
63. $R^1 = CH_3$，$R^2 = OCH_3$
64. $R^1 = CH_2OH$，$R^2 = OCH_3$
65. R^1 = CHO，$R^2 = OCH_3$
66. $R^1 = COOCH_3$，$R^2 = OCH_3$
67. $R^1 = COOCH_3$，R^2 = H



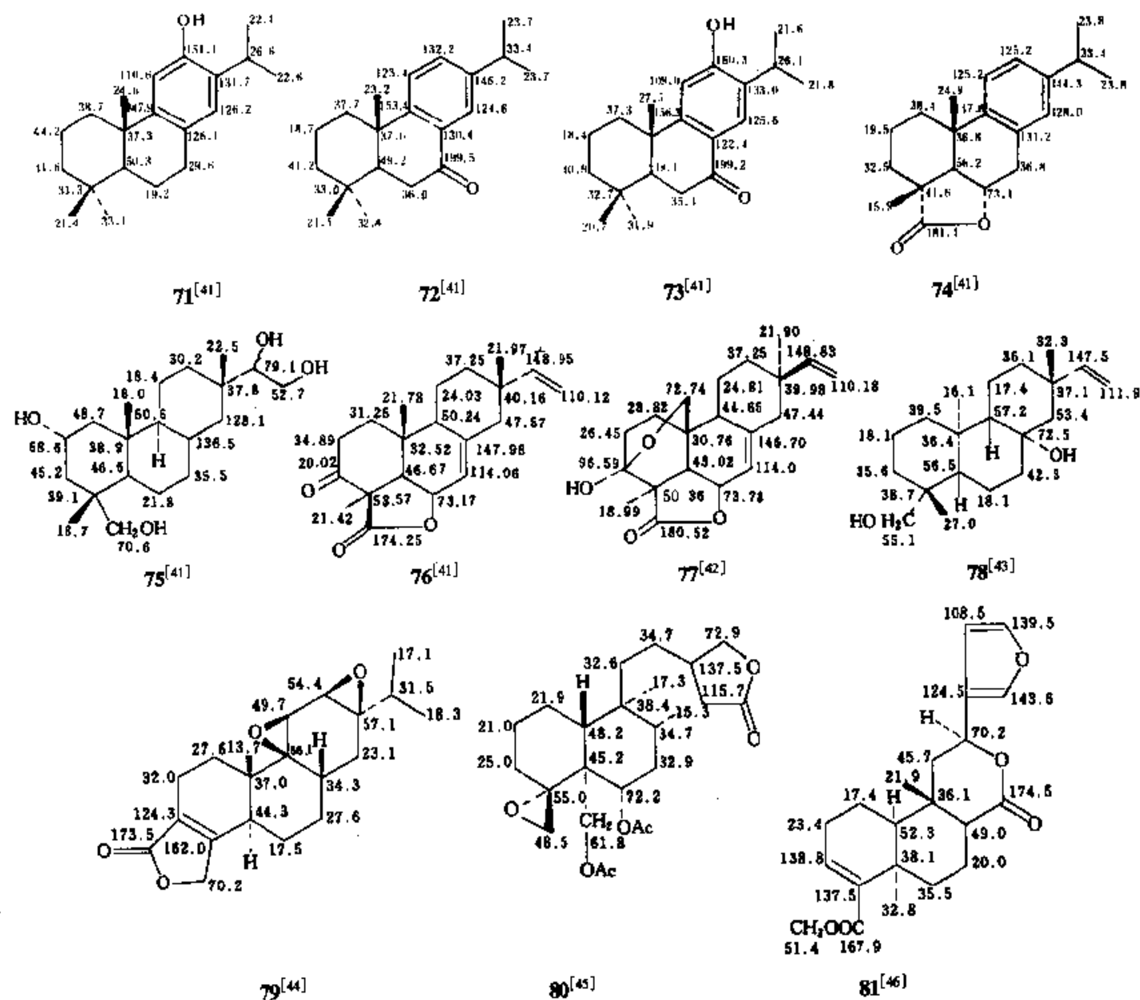
68



69



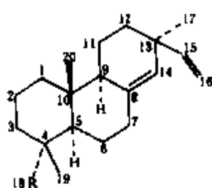
70



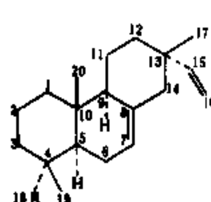
四、三环二萜烯的¹³C-NMR 化学位移

表 21-28　三环二萜烯化合物 82～90 的¹³C-NMR 化学位移数据[56]

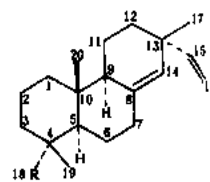
C \ 化合物	82	83	84	85	86	87	88	89	90
1	38.3	39.6	39.7 (t)	38.4	38.6	39.2	39.8 (t)	39.7	40.1
2	18.5	18.5	18.4 (t)	18.3	18.5	17.9	19.6 (t)	19.4	19.0
3	35.5	35.8	35.2 (t)	37.1	37.5	37.2	38.2 (t)	42.5	42.5
4	37.9	37.6	37.7 (s)	47.2	47.6	46.4	43.8 (s)	33.5	33.1
5	47.5	43.7	45.9 (d)	48.7	49.1	45.4	51.0 (d)	55.2	50.5
6	22.5	23.5	22.9 (t)	24.9	15.5	25.7	24.4 (t)	22.9	23.5
7	33.5	121.5	121.3 (d)	35.5	35.5	121.3	121.1 (d)	36.3	121.5
8	138.1	135.3	135.2 (s)	136.2	138.5	135.6	134.4 (s)	138.8	135.2
9	51.5	52.0	52.0 (d)	50.7	51.9	52.4	51.6 (d)	51.8	52.2
10	38.8	35.4	35.2 (s)	38.1	38.1	35.5	35.6 (s)	38.8	35.6
11	19.3	20.5	20.3 (t)	18.8	19.5	20.5	20.9 (t)	19.1	20.3
12	36.0	36.5	36.0 (t)	34.6	36.0	36.0	36.3 (t)	36.3	36.4
13	39.0	36.9	36.8 (s)	37.4	39.0	37.5	36.8 (s)	38.8	37.0
14	128.1	46.4	45.9 (t)	129.3	128.2	46.5	46.1 (t)	128.1	46.3
15	147.0	150.0	149.9 (d)	149.9	147.8	150.7	149.9 (d)	147.7	149.9
16	113.1	109.5	108.9 (t)	110.5	113.2	109.7	109.0 (t)	112.9	109.5
17	29.8	21.8	21.4 (q)	26.2	29.2	21.9	21.4 (q)	29.8	21.8
18	71.7	71.9	26.9 (q)	185.3	185.7	183.9	28.9 (q)	34.5	33.9
19	18.3	18.5	64.7 (t)	16.8	17.6	17.5	177.4 (s)	22.5	22.6
20	15.6	15.9	16.1 (q)	15.3	15.4	15.7	14.1 (q)	14.9	15.2



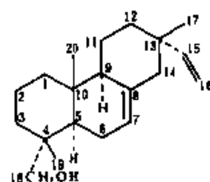
82. R = CH_2OH
85. R = COOH
89. R = CH_3



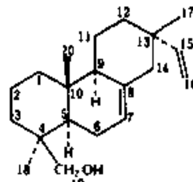
87. R = COOH
90. R = CH_3



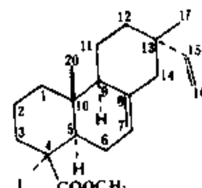
86. R = COOH



83



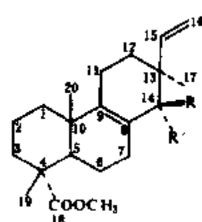
84



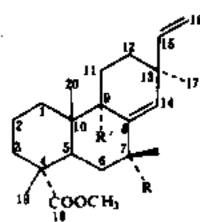
88

表 21-29 三环二萜烯化合物 91～97 的^{13}C-NMR 化学位移数据[57]

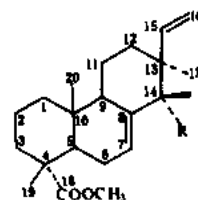
C \ 化合物	91	92	93	94	95	96	97
1	36.0	38.3	38.8	36.0	35.7	38.2	31.8
2	18.3	18.2	18.0	18.3	18.3	8.1	17.9
3	36.8	37.1	37.1	36.6	36.7	37.0	36.6
4	47.8	47.5	46.6	47.8	47.8	47.0	47.5
5	46.4	49.2	45.0	45.9	46.1	42.1	40.1
6	21.7	24.9	25.2	21.2	21.7	32.0	24.6
7	32.1	35.4	125.7	(28.6)	(29.8)	72.7	31.0
8	124.6	138.0	139.6	127.8	126.9	140.6	138.5
9	136.1	51.8	47.2	140.3	140.2	47.0	75.0
10	37.0	37.9	34.9	37.2	37.1	38.2	41.5
11	20.6	19.1	19.9	20.5	20.8	18.5	27.0
12	34.0	35.7	31.2	(31.3)	(26.4)	35.4	32.3
13	34.8	38.7	40.8	39.9	39.7	38.6	39.0
14	42.2	128.5	79.6	76.5	74.9	133.6	131.5
15	149.1	147.4	144.6	146.1	145.9	146.7	145.5
16	109.7	113.0	113.3	112.3	113.4	113.3	112.9
17	23.4	29.5	24.8	18.5	21.2	29.2	29.3
18	179.2	179.4	179.1	179.2	179.3	179.0	179.4
19	16.6	17.1	17.3	16.6	16.5	17.0	17.2
20	19.7	15.1	15.1	19.7	19.9	14.4	17.9
21	51.7	51.6	51.9	51.9	51.9	51.9	51.9



91. R = R′ = H
94. R = H, R′ = OH
95. R = OH, R′ = H



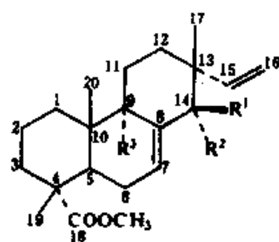
92. R = R′ = H
96. R = OH, R′ = H
97. R = H, R′ = OH



93. R = OH

表 21-30　三环二萜烯化合物 98～114 的^{13}C-NMR 化学位移数据[57]

C \ 化合物	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114
1	39.0	35.8	38.3	38.8	39.1	35.5	35.5	38.2	31.8	32.1	35.2	24.5	23.7	24.3	24.2	24.9	24.4
2	18.1	18.3	18.2	18.1	18.1	18.3	18.1	18.2	18.1	17.9	18.3	19.3	19.2	19.1	19.2	19.5	19.1
3	37.1	36.8	36.9	37.0	37.0	36.5	36.5	36.9	36.6	36.8	36.3	34.8	34.9	34.6	35.0	35.5	34.8
4	46.6	47.8	47.4	46.6	46.7	47.3	47.3	47.0	47.5	46.4	47.3	47.4	47.3	47.0	47.2	47.5	47.2
5	45.3	46.6	49.1	44.9	44.9	41.4	44.4	42.1	40.1	38.0	41.6	128.3	127.7	126.5	125.1	128.8	126.2
6	25.3	21.7	24.9	25.3	25.0	31.2	32.4	31.9	24.5	24.9	28.1	26.0	26.2	36.6	(35.6)	22.1	32.7
7	121.2	32.0	35.5	126.9	118.7	69.0	72.6	72.7	31.2	125.2	71.8	25.7	23.2	67.6	70.8	31.4	70.8
8	135.6	124.7	136.4	137.8	136.5	127.3	127.6	139.2	137.1	136.1	123.2	38.1	41.7	45.0	41.4	73.2	42.2
9	52.1	136.6	50.5	47.1	51.7	141.1	140.7	46.0	74.9	74.4	144.3	37.1	36.9	39.0	36.7	41.7	39.1
10	35.2	37.1	37.8	35.0	35.4	38.0	37.9	38.1	41.4	40.3	37.8	139.0	139.4	139.0	139.1	138.2	139.1
11	20.1	21.1	18.5	19.4	19.8	20.9	21.4	18.2	26.9	25.6	21.4	31.9	31.4	32.1	34.0	26.6	32.1
12	36.2	35.1	34.4	27.6	35.6	34.6	34.6	34.3	31.6	30.7	34.5	33.1	28.5	32.6	32.9	31.8	32.7
13	36.8	35.1	37.3	41.0	42.8	34.9	34.9	37.4	37.9	36.9	35.1	37.3	41.3	36.6	37.3	35.8	36.6
14	46.2	42.1	128.8	79.7	76.9	39.3	37.5	134.0	132.3	43.1	38.5	41.3	80.2	34.6	(38.2)	45.9	34.5
15	150.3	146.3	148.5	146.7	147.5	146.1	145.6	148.1	148.5	150.0	145.6	147.3	145.8	146.8	146.9	149.1	146.6
16	109.4	110.9	109.9	113.3	113.2	111.4	111.3	110.9	110.6	109.6	111.6	111.9	112.8	112.2	112.2	108.2	112.3
17	21.5	27.9	26.0	22.0	14.4	27.7	28.7	25.8	24.0	21.0	28.1	31.5	26.2	31.6	31.5	31.8	31.6
18	179.1	179.4	178.8	179.0	179.2	178.9	179.1	178.8	179.5	179.2	178.5	178.3	178.6	178.1	178.4	178.5	177.9
19	17.5	16.6	17.0	17.5	17.5	16.5	16.5	17.0	17.2	17.5	16.5	23.2	23.2	23.1	23.1	22.9	23.1
20	15.3	19.7	15.2	15.2	15.5	18.3	19.9	14.6	18.3	17.6	18.4	17.2	20.1	18.3	19.7	22.9	18.2
21	51.8	51.8	51.7	51.9	51.9	52.0	52.0	51.9	51.9	52.0	51.7	51.7	51.7	51.9	51.8	52.2	51.9
—$COCH_3$											171.1						171.0
—$COCH_3$											21.4						21.2

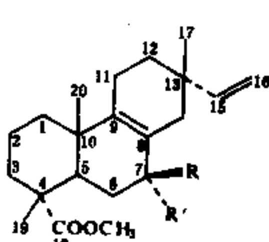


98. $R^1 = R^2 = R^3 = H$

101. $R^1 = H$, $R^2 = OH$, $R^3 = H$

102. $R^1 = OH$, $R^2 = R^3 = H$

107. $R^1 = R^2 = H$, $R^3 = OH$

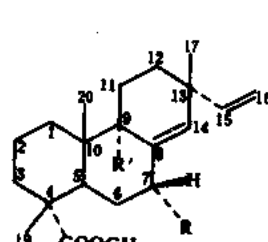


99. $R = R' = H$

103. $R = H$, $R' = OH$

104. $R = OH$, $R' = H$

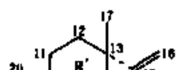
108. $R = H$, $R' = OCOCH_3$



100. $R = R' = H$

105. $R = OH$, $R' = H$

106. $R = H$, $R' = OH$

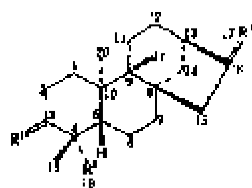


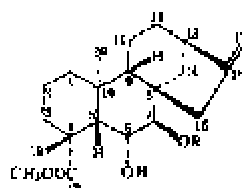
111. $R = H, R' = OH$

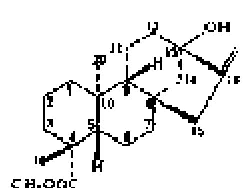
五、四环二萜化合物的^{13}C-NMR 化学位移

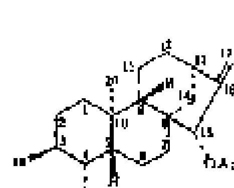
表 21-31 四环二萜 115～123 的^{13}C-NMR 化学位移数据[47]

C \ 化合物	115	116	117	118	119	120	121	122	123
1	41.3	41.0	39.0	41.0	38.9	39.0	40.6	40.8	42.0
2	19.7	18.5	33.9	18.7	19.6	19.6	19.1	19.1	18.5
3	42.0	41.9	217.1	37.6	38.9	39.0	38.0	38.9	42.0
4	33.3	33.2	47.0	43.7	46.1	45.3	43.7	43.7	33.2
5	56.1	56.1	53.6	53.9	49.0	50.1	53.8	47.0	56.2
6	20.3	19.2	20.3	20.7	70.9	67.9	21.8	21.4	20.4
7	40.4	40.3	39.9	40.6	79.0	80.1	39.2	37.7	40.3
8	44.2	42.5	42.2	42.4	46.2	45.1	41.6	46.0	45.3
9	56.1	55.0	54.2	56.7	51.4	52.7	56.9	56.5	56.8
10	39.3	39.4	38.5	39.7	38.7	38.3	39.2	39.4	39.3
11	18.3	18.5	19.0	18.7	18.1	18.1	20.4	18.0	18.0
12	33.3	29.7	29.2	29.5	33.4	33.2	41.3	33.3	26.9
13	44.2	47.9	47.6	47.7	43.8	43.8	80.3	40.6	49.0
14	39.9	37.5	36.9	37.3	42.5	42.6	46.9	36.4	37.7
15	49.2	55.2	54.6	54.9	45.4	45.6	47.4	81.6	58.0
16	156.0	222.5	221.5	222.7	154.3	153.9	155.9	153.7	79.4
17	102.8				103.3	103.4	102.9	106.1	24.5
18	33.7	33.6	37.3	28.9	28.9	29.1	28.6	28.9	33.5
19	21.7	21.7	21.0	184.2	181.4	181.0	177.9	184.6	21.6
20	17.6	18.0	18.1	16.1	18.5	18.4	15.2	15.9	18.0
OCH_3					52.8	52.7	51.1		









115. $R^1 = H_2, R^2 = Me, R^3 = CH_2$
116. $R^1 = H_2, R^2 = Me, R^3 = O$
117. $R^1 = O, R^2 = Me, R^3 = O$
118. $R^1 = H_2, R^2 = CO_2H, R^3 = O$
123. $R^1 = H_2, R^2 = Me,$
$R^3 = \alpha - OH, \beta$-Me

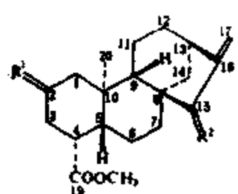
119. R = H
120. R = Ac

121

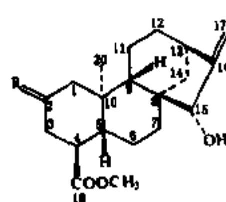
122

表 21-32　四环二萜 124～132 的^{13}C-NMR 化学位移数据[47]

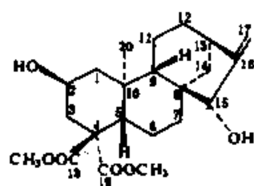
C \ 化合物	124	125	126	127	128	129	130	131	132
1	49.0	48.2	56.1	55.2	55.3	48.3	47.6	49.9	45.0
2	63.8	65.8	208.5	208.9	207.8	64.0	63.8	202.2	67.7
3	37.3	39.1	42.8	43.6	43.0	37.4	42.6	53.4	33.5
4	43.8	43.9	45.3	45.1	45.3	43.7	58.6	42.3	43.3
5	49.0	48.7	48.3	47.7	47.5	48.3	53.1	48.2	48.6
6	25.4	22.7	24.9	23.0	24.1	24.4	23.1	24.2	24.0
7	34.8	33.7	34.3	33.2	32.8	33.2	34.8	34.1	34.8
8	47.4	47.3	47.4	47.7	51.7	52.2	48.7	47.3	44.5
9	51.2	51.4	51.7	50.4	50.2	50.8	51.0	51.6	51.5
10	40.3	39.8	42.0	42.0	43.0	40.8	40.0	43.3	40.3
11	18.2	18.2	18.1	18.1	18.1	18.2	18.3	18.0	18.8
12	32.4	32.3	32.1	32.1	31.7	32.0	32.5	32.0	29.4
13	42.1	42.0	42.0	42.0	37.9	38.0	42.2	41.9	46.8
14	36.2	36.5	35.6	35.8	35.9	36.5	36.3	35.6	33.5
15	82.4	82.6	82.2	82.2	209.6	210.3	82.4	82.0	80.3
16	159.4	159.6	159.6	159.3	148.9	149.1	159.5	159.2	216.8
17	108.5	108.7	108.7	108.0	115.1	114.9	108.7	108.8	
18		175.8		174.9			172.7		
19	175.6		173.0		175.4	175.3	172.7	171.5	174.3
20	16.4	16.5	17.0	16.9	16.7	16.2	17.0	16.7	16.8
OCH_3	52.8	51.4	52.1	52.0	51.7	51.4	52.1;52.8	52.1	52.7



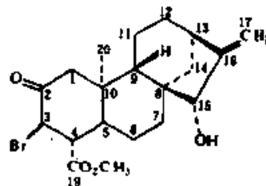
124. R^1 = H, β-OH, R^2 = α-OH, H
126. R^1 = O, R^2 = α-OH, H
128. R^1 = R^2 = O
129. R^1 = H, β-OH, R^2 = O



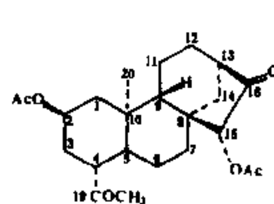
125. R = H, β-OH
127. R = O



130



131

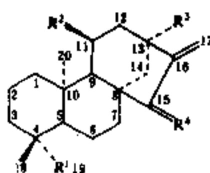


132

表 21-33 四环二萜 133 ~ 143 的^{13}C-NMR 化学位移数据[51]①

化合物 / C	133	134	135	136	137	138	139	140	141	142	143
1	40.5(40.5)	41.1	40.8(40.9)	41.1	40.0(39.9)	40.9(40.9)	40.9(40.7)	40.2	40.9	41.1	41.0(40.9)
2	18.9[b](18.7)[b]	19.8	19.5(19.2)	19.8	19.3(18.8)	19.6(19.2)	19.6(19.2)	19.6	19.9	19.8	19.4[b](19.2)[b]
3	42.2(42.1)	38.6	38.2(38.1)	38.6	38.3(38.0)	38.3(38.1)	38.3(38.1)	38.5	38.5	38.7	38.3(38.2)
4	33.3(33.3)	43.8	43.9(43.9)	43.9	43.9(43.7)	44.0(43.9)	44.0(43.9)	43.9	44.0	43.9	44.0(43.9)
5	56.2[c](56.3)[c]	57.1	56.9(57.2)	57.1	56.2(56.1)	57.1(57.1)	56.7(56.4)	56.4	56.7	57.0	56.8(56.9)
6	20.4(20.3)	22.5	22.2(21.9)	22.6	20.6(20.0)	21.7(21.1)	22.2(21.6)	20.9	22.3	22.9	21.3(21.0)
7	41.3(41.3)	41.5	41.4(41.4)	41.8	30.6[b](36.4)[b]	36.6[b](36.3)[b]	36.8(36.3)	37.3	36.5	42.7	44.0(43.9)
8	44.3(44.3)	44.4	44.4(44.3)	41.8	52.5(52.3)	48.2(47.8)	46.3(45.7)	51.0	45.4	44.9	49.5(49.2)
9	56.1[c](56.1)[c]	55.2	55.1(55.2)	54.3	51.8(51.5)	54.0(53.5)	46.0(45.5)	63.3	55.3	56.3	48.2(48.1)
10	39.5(39.4)	39.9	39.6(39.5)	39.8	40.3(40.6)	39.9(39.7)	39.4(39.1)	39.3	38.3	40.0	39.7(39.6)
11	18.3[b](18.2)[b]	18.6	18.6(18.4)	20.8	18.7(18.2)	18.7(18.3)	18.3(18.3)	65.3	65.7	18.9	19.2[b](19.0)[b]
12	33.5(33.3)	33.3	33.3(33.2)	40.7	32.4(32.1)	33.1(32.6)	33.9(33.1)	41.6	42.6	26.8	25.1(24.9)
13	44.3(44.0)	44.2	44.2(43.9)	79.8	38.3(38.0)	42.8(42.3)	40.7(40.1)	37.8	39.9	45.8	45.0(44.8)
14	40.0(39.9)	39.9	39.8(39.7)	47.4	34.1[b](33.6)[b]	36.2[b](35.3)[b]	39.4(38.9)	34.9	39.4	37.8	39.7(39.6)
15	49.9(49.2)	49.2	49.1(49.0)	48.1	209.6(210.3)	82.6(82.7)	82.2(82.5)	208.8	82.9	53.9	135.6(135.1)
16	155.8(156.0)	155.7	155.7(155.8)	157.6	150.2(149.4)	161.1(160.3)	159.6(158.4)	151.9	159.4	81.6	142.2(142.5)
17	103.4(102.8)	103.5	103.6(103.1)	102.9	113.9(114.2)	107.8(108.2)	104.4(104.7)	110.8	105.6	66.4	15.4(15.2)
18	33.7(33.7)	29.3	28.6(28.8)	29.3	28.6(28.5)	28.7(28.8)	28.7(28.7)	29.3	29.3	29.3	28.7(28.7)
19	21.2(21.7)	179.9	177.5(178.0)	180.0	177.5(177.7)	177.7(178.0)	177.7(178.0)	179.9	180.0	180.1	177.6(178.0)
20	17.7(17.6)	16.0	15.5(15.4)	15.9	15.5(15.3)	15.9(15.7)	15.8(15.5)	16.0	15.9	15.4	15.4(15.2)
$COOCH_3$			51.1(51.1)		51.2(51.0)	51.1(51.2)	51.1(51.1)				51.1(51.1)

① b、c 表示数据可以互换。



133. $R^1 = CO_3, R^2 = H, R^3 = H, R^4 = H_2$

134. $R^1 = CO_2H, R^2 = H, R^3 = H, R^4 = H_2$

135. $R^1 = CO_2Me, R^2 = H, R^3 = H, R^4 = H_2$

136. $R^1 = CO_2H, R^2 = H, R^3 = OH, R^4 = H_2$

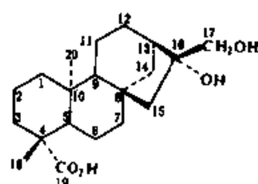
137. $R^1 = CO_2Me, R^2 = H, R^3 = H, R^4 = O$

138. $R^1 = CO_2Me, R^2 = H, R^3 = H, R^4 =$ <(H)(OH)

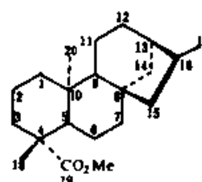
139. $R^1 = CO_2Me, R^2 = H, R^3 = H, R^4 =$ <(OH)(H)

140. $R^1 = CO_2H, R^2 = OH, R^3 = H, R^4 = O$

141. $R^1 = CO_2H, R^2 = OH, R^3 = H, R^4 =$ <(OH)(H)



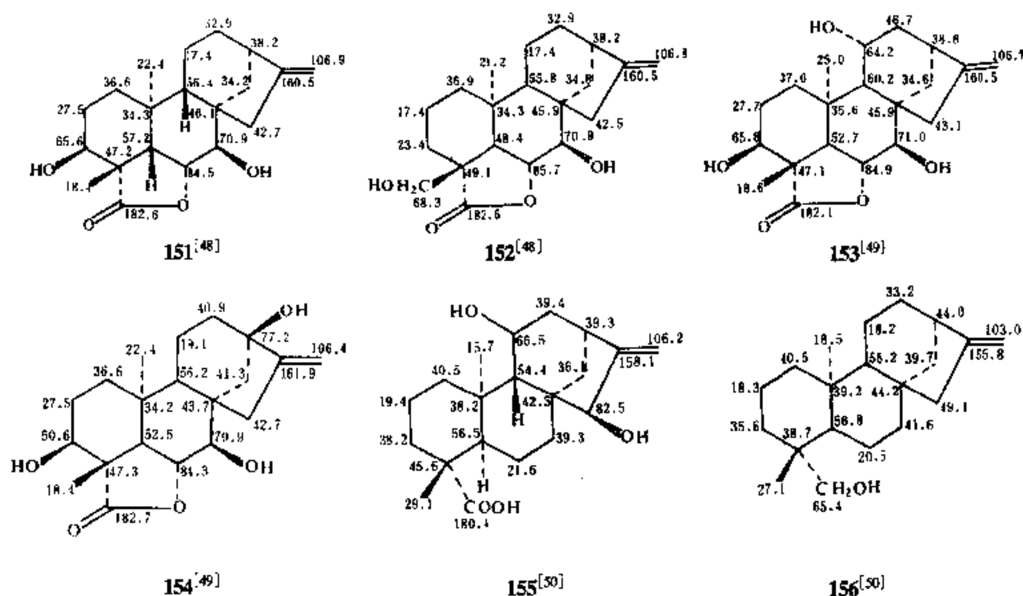
142



143

表 21-34　四环二萜 144～150 的^{13}C-NMR 化学位移数据[56]

C \ 化合物	144	145	146	147	148	149	150
1	42.0 (t)	41.9 (t)	40.0 (t)	41.4 (t)	42.0 (t)	41.1	41.3
2	18.2 (t)	18.7 (t)	19.3 (t)	18.5 (t)	18.6 (t)	19.8	18.7
3	42.0 (t)	42.0 (t)	41.9 (t)	42.0 (t)	43.8 (t)	38.7	42.0
4	33.4 (s)	33.2 (s)	33.2 (s)	33.1 (s)	33.2 (s)	43.9	33.3
5	56.1 (d)	56.1 (d)	55.8 (d)	56.0 (d)	48.3 (d)	57.0	56.1
6	20.5 (t)	20.0 (t)	20.1 (t)	20.4 (t)	19.2 (t)	22.9	20.3
7	37.2 (t)	38.2 (t)	38.5 (t)	36.8 (t)	39.2 (t)	42.7	40.4
8	44.6 (s)	43.5 (s)	45.3 (s)	44.3 (s)	48.8 (s)	44.9	44.2
9	56.7 (d)	56.9 (d)	56.1 (d)	56.0 (d)	55.8 (d)	56.3	56.1
10	39.4 (s)	39.3 (s)	39.2 (s)	39.2 (s)	39.4 (s)	40.0	39.3
11	18.3 (t)	18.6 (t)	18.6 (t)	18.3 (t)	18.6 (t)	18.9	18.1
12	26.3 (t)	26.7 (t)	29.1 (t)	25.9 (t)	25.6 (t)	26.8	33.3
13	45.5 (d)	52.6 (d)	42.6 (d)	48.8 (d)	41.1 (d)	45.8	44.2
14	40.4 (t)	40.4 (t)	40.3 (t)	40.2 (t)	40.4 (t)	37.8	39.9
15	53.4 (t)	56.1 (t)	48.8 (t)	56.6 (t)	135.7 (d)	53.9	49.2
16	81.6 (s)	79.7 (s)	66.2 (s)	86.7 (s)	145.6 (s)	81.6	156.0
17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

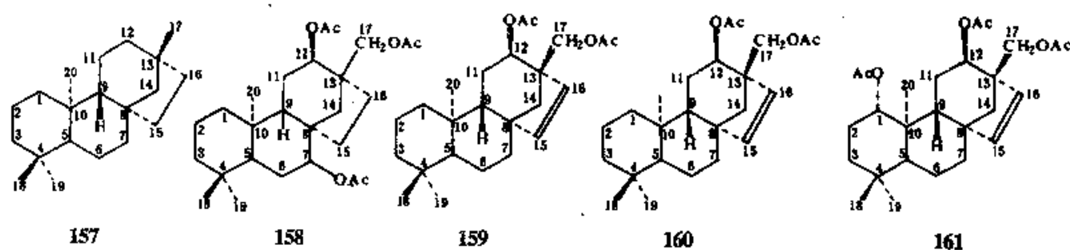


151[48]　152[48]　153[49]

154[49]　155[50]　156[50]

表 21-35　四环二萜 157~161 的^{13}C-NMR 化学位移数据[52]

化合物 C	157	158	159	160	161	化合物 C	157	158	159	160	161
1	39.7	39.3	38.2	38.6	81.5	11	20.2	25.1	26.4	26.1	28.7
2	18.5	18.2	18.4	18.3	24.9	12	40.0	72.4	68.9	68.4	68.8
3	42.0	41.8	41.9	41.9	39.2	13	39.2	46.3	50.8	51.1	50.5
4	33.1	32.5	33.1	32.5	32.9	14	57.7	41.6	49.2	44.9	48.9
5	56.5	47.7	55.8	47.8	54.9	15	33.6	32.2	139.3	136.6	138.8
6	20.4	25.0	20.0	25.2	19.7	16	37.6	30.4	131.4	133.1	131.9
7	41.2	78.2	36.4	75.2	36.6	17	27.1	67.5	65.5	65.2	65.3
8	44.9	47.4	48.3	52.0	48.6	18	33.7	33.3	33.5	33.2	32.9
9	56.9	48.5	49.3	44.9	49.2	19	21.9	21.6	21.8	21.6	21.5
10	37.6	37.3	36.9	36.9	41.6	20	15.1	14.7	14.2	13.7	10.5



157　158　159　160　161

六、四环二萜甙的^{13}C-NMR 化学位移

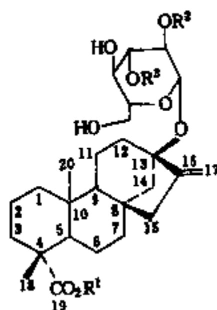
表 21-36　四环二萜甙 162~169 的^{13}C-NMR 化学位移数据[51]

化合物 C	162	163	164	165	166	167	168	169
1	41.0	40.9	40.7	41.0	40.9	40.8	40.5	39.9
2	19.7	19.7	19.2	19.8	19.4	19.6	19.5	19.2
3	38.4	38.5	38.1	38.7	38.3	38.4	38.3	38.1
4	43.8	43.8	43.9	43.8	44.0	44.2	44.1	44.0

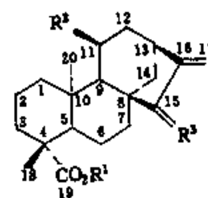
续表

化合物 C	162	163	164	165	166	167	168	169
5	56.9	56.9	57.3	57.0	57.4	57.2	57.1	56.8
6	22.5	22.4	22.0	22.5	22.2	22.0	21.8	20.5
7	41.6	41.5	41.5	41.8	41.8	36.7	36.3	37.0
8	42.1	42.4	42.5	42.2	42.4	46.3	45.4	50.8
9	54.1	54.1	53.8	54.1	54.0	46.1	55.2	63.1
10	39.7	39.6	39.7	39.8	39.8	39.6	38.3	39.2
11	20.6	20.5	20.6	20.6	20.7	18.4	65.7	65.3
12	38.4	37.2	36.6	37.8	37.3	33.8	42.5	41.4
13	86.4	86.1	85.9	86.8	86.6	40.7	39.9	37.7
14	44.6	44.7	44.3	44.5	44.5	39.6	39.9	34.8
15	48.2	47.9	47.5	47.9	47.9	82.3	82.8	208.8
16	153.7	154.0	154.3	153.7	153.9	159.7	159.4	151.8
17	104.9	104.9	104.5	104.6	104.5	104.3	105.5	110.7
18	29.2	29.2	28.2	29.3	28.3	28.6	28.6	28.5
19	180.0	180.1	177.0	180.2	177.0	176.9	176.8	176.6
20	15.7	15.9	15.4	16.1	15.5	16.1	15.7	15.8
G①-1			95.6		95.6	95.7	95.7	95.7
2			73.8		73.8	74.0	73.9	73.9
3			79.0		78.8	79.0	79.2	79.2
4			70.8		70.8	71.1	71.1	71.0
5			79.0		78.8	79.0	79.2	79.0
6			61.9		62.3	62.1	62.1	62.1
G1-1	99.4	97.6	97.7	97.8	97.9			
2	75.3	84.1	84.3	80.5	80.7			
3	(77.9)	(77.6)	77.9	88.0	87.8			
4	71.5	71.1	(71.3)	69.8	70.5			
5	(78.5)	(77.8)	77.9	(78.4)	(78.3)			
6	62.5	62.3	62.5	(62.3)	(62.3)			
G2-1		106.2	106.5	(104.4)	(104.5)			
G3-1				(104.6)	104.5			

① G = Glu。



162. $R^1 = R^2 = R^3 = H$
163. $R^1 = R^3 = H$, $R^2 = Glu$
164. $R^1 = R^2 = Glu$, $R^3 = H$
165. $R^1 = R^2 = R^3 = Glu$
166. $R^1 = R^2 = R^3 = Glu$

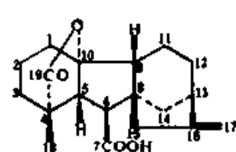


167. $R^1 = Glu$, $R^2 = H$, $R^3 =$ <(OH)(H)
168. $R^1 = Glu$, $R^2 = OH$, $R^3 =$ <(OH)(H)
169. $R^1 = Glu$, $R^2 = OH$, $R^3 = O$

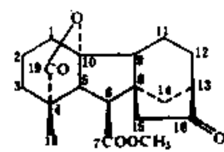
七、五环二萜内酯的^{13}C-NMR 化学位移

表 21-37　五环二萜内酯 170～179 的^{13}C-NMR 化学位移数据[53]

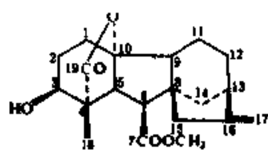
C \ 化合物	170	171	172	173	174	175	176	177	178	179
1	30.7	30.4	27.4	27.1	30.6	25.5	132.1	132.4	129.1	129.2
2	19.4	19.2	28.1	28.1	34.9	27.7	133.2	132.9	134.2	134.2
3	34.3	34.2	70.2	69.9	199.8	71.3	69.9	69.8	70.2	70.3
4	49.1	49.0	54.6	54.7	53.1	53.1	53.4	53.5	52.1	52.2
5	58.0	57.8	51.6	51.1	56.7	53.0	52.2	52.2	53.4	53.4
6	51.8	52.9	51.1	52.7	52.8	50.2	50.5	50.2	50.5	50.4
7	178.0	172.5	173.4	172.6	173.6	172.5	175.8	173.1	172.3	172.3
8	51.3	49.7	51.6	49.8	51.3	51.0	52.2	52.4	50.5	51.0
9	53.9	54.1	53.7	53.9	53.4	52.5	51.7	51.6	50.9	51.0
10	93.6	92.9	94.2	93.9	92.5	92.8	90.9	91.1	90.2	90.0
11	16.1	16.7	16.1	16.8	16.9	17.0	16.0	15.9	16.9	16.9
12	31.4	24.9	31.5	25.0	24.9	36.3	31.4	31.4	38.3	36.4
13	38.8	44.7	38.9	44.8	44.5	84.3	38.6	38.6	78.0	84.1
14	36.8	34.5	36.8	34.6	34.6	40.2	36.5	36.4	43.1	39.8
15	44.3	50.4	44.5	50.5	50.2	42.2	44.4	44.5	44.7	42.7
16	156.5	220.1	156.8	220.6	219.3	153.4	156.4	156.5	156.7	153.4
17	107.5		107.5			107.9	107.8	107.7	107.6	108.2
18	17.2	17.1	14.7	14.6	10.3	14.5	14.6	14.4	14.3	14.3
19	179.6	178.8	178.6	178.6	171.5	176.3	178.5	178.9	177.0	176.9



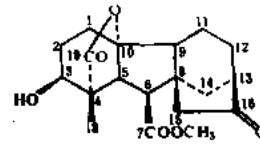
170



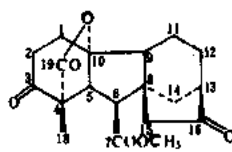
171



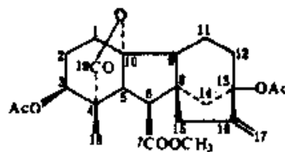
172



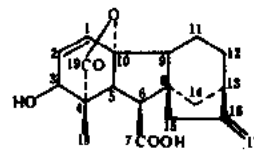
173



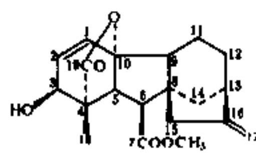
174



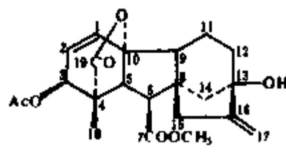
175



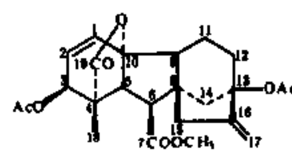
176



177



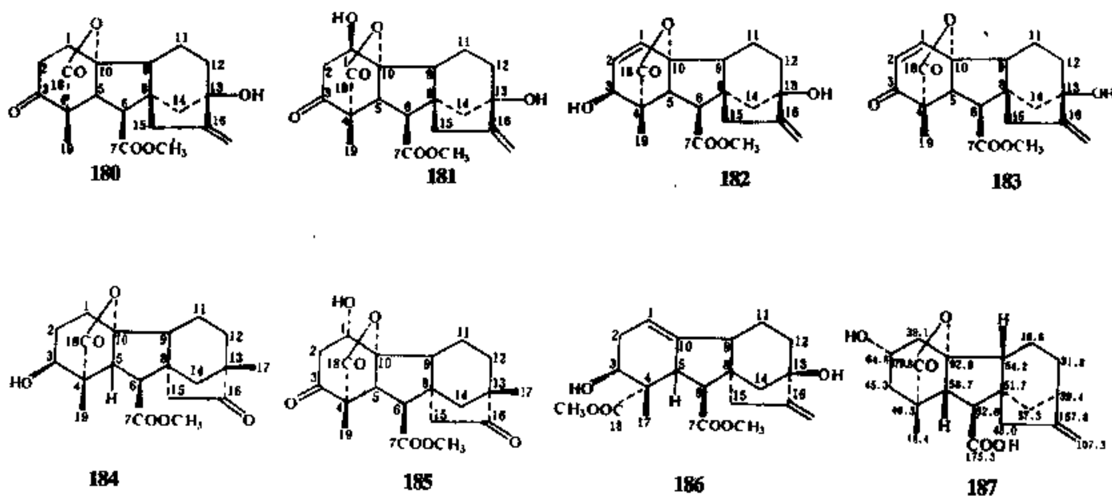
178



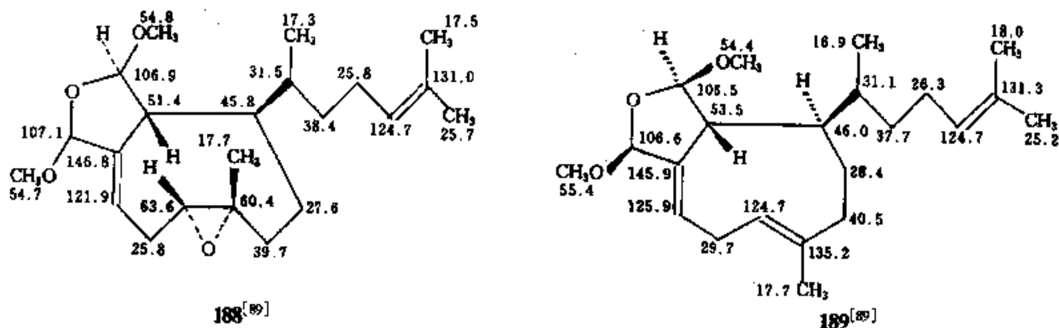
179

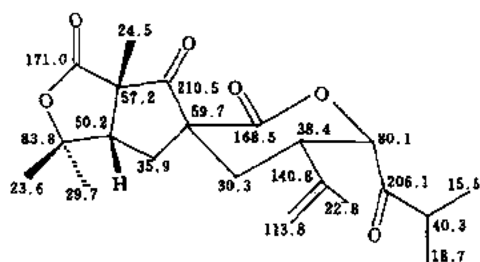
表 21-38　五环二萜内酯 180～186 的^{13}C-NMR 化学位移数据[54]

化合物 / C	180	181	182	183	184	185	186
1	30.8	65.9	133.0	149.3	26.4	71.6	111.7
2	35.2	45.1	133.5	129.1	28.6	45.7	33.1
3	201.9	200.9	69.9	193.1	70.9	203.8	70.5
4	63.7	64.1	54.1	65.5	54.0	61.3	49.2
5	57.5	53.0	53.4	62.4	51.0	55.2	46.9
6	51.9	51.4	51.4	51.4	53.1	52.9	50.6
7	173.0	173.0	173.3	172.4	174.5	173.5	175.5
8	51.9	53.8	51.0	50.4	51.6	51.3	50.7
9	52.8	47.0	51.4	52.1	54.0	50.7	47.1
10	93.8	95.4	91.4	90.8	93.4	94.4	141.6
11	18.2	17.8	17.6	17.5	19.9	21.9	19.4
12	39.5	39.6	39.6	39.3	36.0	35.9	38.9
13	78.1	78.2	78.2	78.1	49.3	51.1	79.3
14	46.1	46.2	45.1	45.1	47.8	47.8	49.5
15	43.2	43.2	43.6	43.2	50.7	50.3	39.7
16	157.8	157.8	158.6	158.1	219.0	218.4	156.1
17	10.7	10.4	14.8	11.7	14.8	10.5	21.6
18	174.8	173.6	173.5	174.2	179.0	174,9	177.0
OCH_3	52.8	52.6	52.4	52.6	52.4	52.6	51/8/52.0

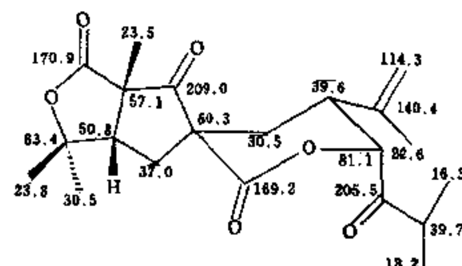


八、其他二萜类化合物的^{13}C-NMR 化学位移





190[90]

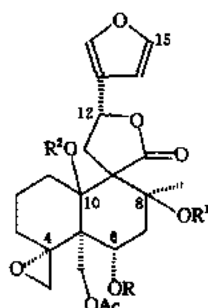


191[90]

表 21-39 二萜化合物 192～194 的^{13}C-NMR 化学位移数据[91]

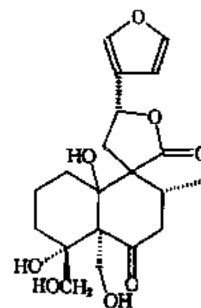
化合物 C	192	193	194①	化合物 C	192	193	194①
1	31.8	30.6	25.4	13	124.9	125.0	119.2
2	18.8	18.9	14.9	14	108.0	108.0	107.3
3	29.4	29.3	21.0	15	144.2	144.1	143.2
4	62.9	63.9	74.8	16	139.6	139.6	139.4
5	49.8	51.6	51.9	17	26.0	26.1	15.3
6	67.3	64.9	197.0	18	51.6	51.6	69.8
7	38.2	39.3	37.7	19	63.6	63.8	59.2
8	75.8	76.0	31.2	20	174.6	174.8	174.2
9	59.3	59.6	53.8	C=O	170.6	170.8	
10	81.9	81.5	84.0	CH_3CO	21.2	21.1	
11	34.8	34.9	33.0	C=O	170.6		
12	72.2	72.1	71.2	CH_3CO	21.2		

① 在 $CDCl_3$ 和氘代丙酮中测定。



192. R = Ac, R¹ = R² = H

193. R = R¹ = R² = H



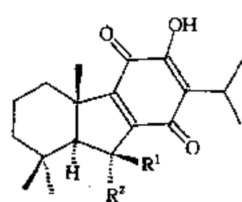
194

表 21-40 二萜类化合物 195～199 的^{13}C-NMR 化学位移数据[92]

化合物 C	195①	196②	197②	198①	199①	化合物 C	195①	196②	197②	198①	199①
1	34.4	35.8	37.6	35.6	30.3	12	151.2	154.3	153.5	146.8	152.2
2	19.3	20.2	20.4	19.7	17.5	13	124.6	125.0	125.6	116.7	126.1
3	41.1	44.1	44.2	41.7	36.5	14	185.3	186.1	187.0	146.0	151.1
4	33.6	35.1	35.2	34.0	34.3	15	24.2	24.9	24.9	25.1	25.9
5	61.5	62.1	69.6	61.5	65.1	16	19.8	20.4	20.5	21.0	20.6
6	200.2	203.7	201.5	205.0	—	17	19.8	20.4	20.5	21.1	20.9
7	54.4	88.4	90.2	54.5	211.1	18	35.0	34.8	33.8	34.4	24.4
8	149.2	148.8	147.4	113.4	118.3	19	21.8	23.7	24.6	22.0	33.0
9	152.8	155.1	154.3	132.3	142.7	20	20.1	22.8	23.9	22.4	28.8
10	48.7	50.2	47.3	46.3	42.7	亚甲二氧基				100.8	
11	181.0	182.8	182.6	135.2	138.4	甲氧基					62.1

① 在 $CDCl_3$ 中测定。

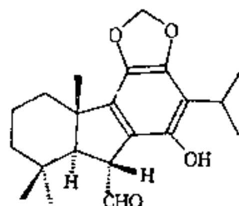
② 在氘代丙酮中测定。



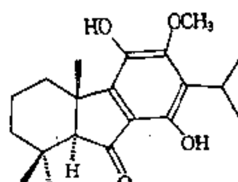
195. R^1 = H, R^2 = CHO

196. R^1 = OH, R^2 = CHO

197. R^1 = CHO, R^2 = OH



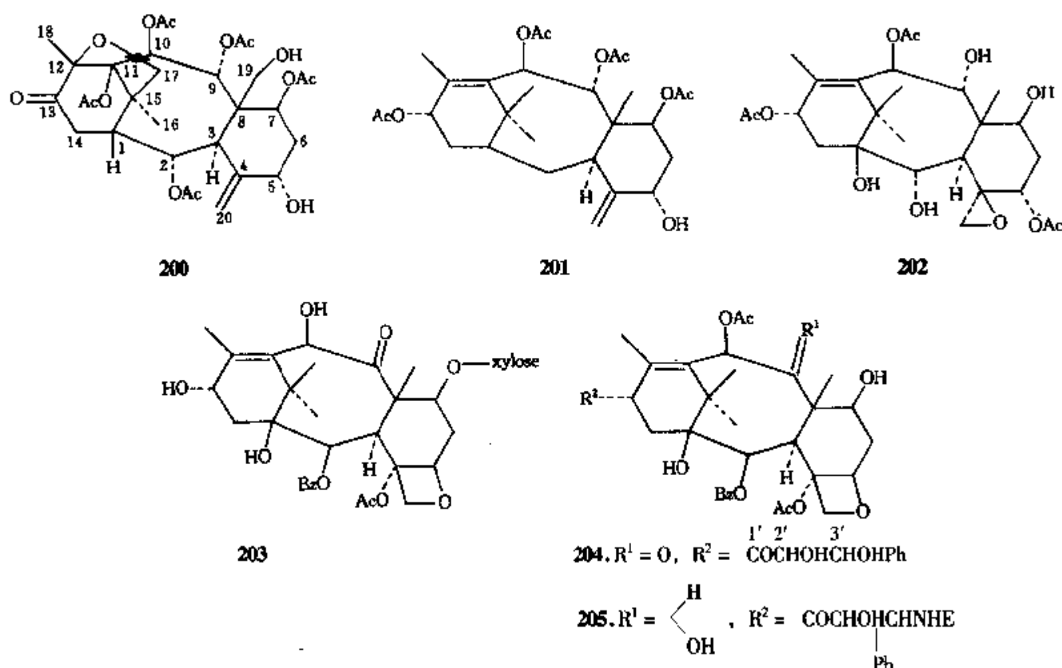
198



199

表 21-41 红豆杉二萜化合物 200 ~ 205 的^{13}C-NMR 化学位移数据[93,94]

C \ 化合物	200	201	202	203	204	205
1	48.93	39.91	75.88	78.38	79.29	78.27
2	69.70	27.05	73.83	75.97	75.06	73.23
3	36.54	35.70	38.71	48.14	45.89	46.82
4	144.8	151.7	60.39	81.24	81.23	82.86
5	72.83	73.44	77.61	84.63	84.43	83.99
6	39.41	36.20	33.17	36.40	35.73	37.79
7	68.76	69.94	69.42	82.59	72.15	73.73
8	49.31	46.68	46.33	57.26	58.73	45.32
9	64.34	76.85	78.41	210.9	203.5	77.10
10	70.47	72.23	74.29	76.26	76.65	73.34
11	80.52	136.1	136.6	135.4	133.2	135.3
12	91.57	137.8	140.2	143.4	141.9	138.3
13	204.4	70.12	71.57	67.42	71.60	71.66
14	34.02	32.47	38.43	40.82	36.05	35.66
15	49.79	39.03	43.08	43.63	43.16	43.11
16	15.19	26.36	22.21	20.64	21.57	22.23
17	82.37	32.22	28.29	27.36	26.81	28.34
18	12.09	15.95	15.43	15.53	14.95	14.99
19	61.58	12.67	13.78	11.24	9.54	12.68
20	112.9	112.4	51.25	76.51	76.48	76.70
OAcCH$_3$	20.63×2	20.77	21.18	20.60	20.76	21.23
	20.77	20.89	21.32		22.40	22.74
	21.20	20.94	21.58			
	21.27	21.37				
C=O	168.0	169.0	169.0	170.4	170.1	170.0
	168.4	169.4	169.8		171.1	170.4
	169.7	169.9	169.9			
	170.3	170.1				
	171.9					
OBzC=O				166.3	167.0	166.7
1″				131.3	129.3	129.2
2″, 6″				128.7	130.1	130.1
3″, 5″				130.2	128.7	128.7
4″				133.1	133.8	133.8
1′					172.1	171.4
2′					75.06	73.64
3′					75.40	54.54
Ph1″					138.8	138.4
2″, 6″					126.2	127.3
3″, 5″					128.8	128.7
4″					128.8	128.1
NBzC=O						166.8
1″						133.9
2″, 6″						127.1
3″, 5″						128.7
4″						131.8

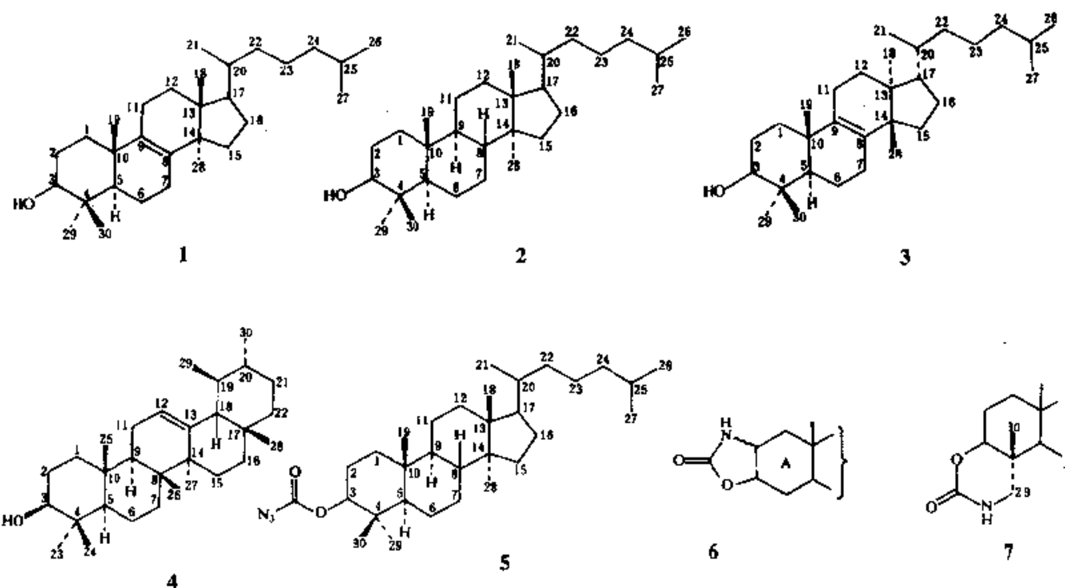


第五节　三萜化合物的^{13}C-NMR 化学位移

一、羊毛脂甾烷类三萜的^{13}C-NMR 化学位移

表 21-42　羊毛脂甾烷类三萜 1～7 的^{13}C-NMR 化学位移数据[58]

C \ 化合物	1	2	3	4	5	6	7
1	35.8	37.7	35.4	38.95	36.76	41.45	36.52
2	27.9	27.7	27.8	27.35	23.63	52.00	23.06
3	79.0	79.1	78.9	78.97	85.74	91.13	81.78
4	39.0	39.0	37.3	38.78	36.65	36.71	34.04
5	50.5	55.1	51.1	55.34	54.56	55.32	52.76
6	19.2	18.3	19.1	18.45	19.90	20.26	19.77
7	28.3	29.0	28.0	33.07	28.48	28.32	28.18
8	134.4	38.7	134.1	40.13	38.22	37.95	38.16
9	134.4	48.8	133.6	47.85	48.06	48.04	48.01
10	37.2	37.2	39.0	36.95	37.79	39.11	36.73
11	21.1	20.1	21.6	23.41	21.20	20.52	21.47
12	26.7	21.7	28.1	124.5	33.26	33.15	33.26
13	44.6	45.3	44.2	139.6	44.80	44.80	11.69
14	49.9	48.0	50.1	42.18	47.41	47.41	17.33
15	31.2	33.7	31.0	26.70	31.77	31.69	31.58
16	31.0	32.2	29.8	28.16	27.73	27.73	27.59
17	50.7	51.1	49.8	33.77	50.50	50.46	50.44
18	15.9	16.3	15.7	59.19	14.21	15.70	13.97
19	18.3	13.9	20.2	39.76	16.10	16.07	14.16
20	36.5	36.2	35.7	39.65	35.82	35.79	35.79
21	18.8	18.7	19.1	31.29	18.48	18.45	18.45
22	36.5	36.7	36.1	41.59	36.25	36.19	36.19
23	24.2	24.1	23.9	28.16	23.87	23.84	23.84
24	39.6	39.6	39.5	15.65	39.13	39.11	39.11
25	28.1	28.0	28.0	15.65	27.73	27.73	27.70
26	22.6	22.6	22.8	16.95	22.60	22.63	22.60
27	22.8	22.8	22.8	23.25	22.33	22.33	22.30
28	24.3	14.4	24.5	28.75	16.40	16.37	16.07
29	28.1	28.3	28.0	17.48	27.83	27.73	54.10
30	15.4	15.6	15.5	21.30	13.78	14.28	12.43
CO					159.80	159.80	153.25



二、环阿尔廷醇类三萜的^{13}C-NMR 化学位移

表 21-43　环阿尔廷醇类三萜 8～15 的^{13}C-NMR 化学位移数据[59]

C \ 化合物	8	9	10	11	12	13	14	15
1	31.9	31.5	33.3	30.7	30.4	32.8	31.4	31.9
2	30.3	26.7	37.2	34.8	30.9	40.8	30.4	30.3
3	78.5	80.3	215.1	76.3	78.5	212.2	73.7	78.5
4	40.3	39.4	50.0	44.5	41.4	49.8	38.5	40.4
5	47.0	47.0	48.3	43.2	43.3	45.9	37.1	47.0
6	21.0	20.8	21.5	24.6	24.6	25.1	28.1	21.1
7	28.0	28.0	27.9	28.0	28.0	28.0	27.8	28.0
8	47.8	47.6	47.7	46.7	46.7	46.9	46.1	47.8
9	20.0	20.1	21.0	23.5	23.6	24.9	23.5	20.0
10	26.0	26.0	26.0	29.5	29.3	29.3	29.3	26.0
11	26.0	25.8	26.0	25.1	24.9	25.8	24.6	26.0
12	35.5	35.4	35.5	35.2	35.3	35.3	35.2	35.5
13	45.1	45.1	45.2	45.2	45.2	45.2	45.3	45.1
14	48.7	48.6	48.5	48.7	48.7	48.7	49.0	48.7
15	32.8	32.8	32.8	32.8	32.8	32.8	32.9	32.9
16	26.5	26.5	26.7	26.9	26.9	26.9	27.1	26.5
17	52.2	52.2	52.2	52.0	52.0	52.1	52.3	52.1
18	17.9	17.9	18.1	17.7	17.7	17.9	17.5	17.9
19	29.8	29.6	29.5	26.9	26.9	27.1	25.7	29.6
20	36.0	36.0	36.0	36.0	36.0	36.0	36.2	36.5
21	18.3	18.3	18.1	18.3	18.3	18.3	18.5	18.4
22	36.4	36.4	36.4	35.0	35.0	35.0	36.5	33.9
23	24.0	24.1	24.1	31.3	31.3	31.3	24.2	31.4
24	39.4	39.4	39.4	156.2	156.1	156.1	39.6	39.0
25	28.0	28.0	27.9	33.7	33.7	33.7	28.1	30.9
26	22.5	22.5	22.5	21.8	21.9	21.8	22.9	20.5
27	22.7	22.7	22.7	21.8	21.9	21.8	22.9	17.6
28	19.3	19.2	19.3	19.5	19.1	19.1	19.0	19.3
29	25.4	25.3	26.0	14.4	14.4	10.7	—	25.4
30	14.0	15.1	20.6	—	—	—	—	14.0
31				105.6	105.6	105.6	—	15.5
$OCOCH_3$		170.0			170.1		170.0	
$OCOCH_3$		21.2			21.2		21.5	

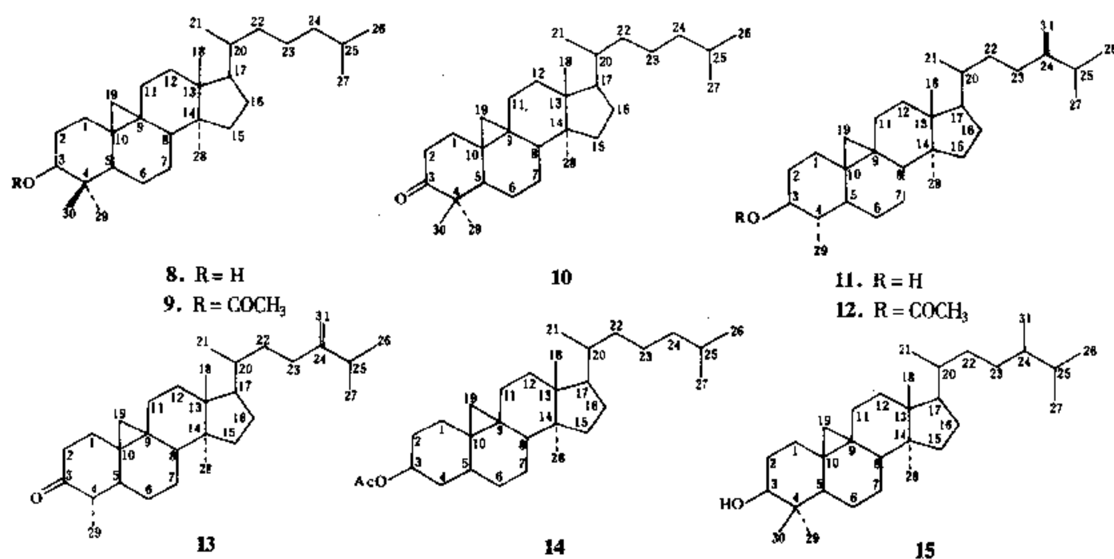


表 21-44 多环三萜化合物 16～22 的^{13}C-NMR 化学位移数据[60]

C \ 化合物	16	17	18	19	20	21	22
1	31.66	31.81	31.91	32.04	31.88	33.67	33.65
2	28.98	30.08	29.18	30.32	26.82	37.37	37.30
3	88.04	77.50	88.12	77.40	79.97	216.30	215.79
4	40.64	40.30	40.70	40.33	39.48	50.26	50.23
5	46.76	46.57	47.16	46.97	47.05	48.40	48.15
6	20.19	20.38	20.64	20.82	20.76	21.35	21.47
7	25.34	25.55	25.73	25.96	26.06	26.44	25.53
8	45.65	45.71	48.13	48.15	47.47	43.08	42.26
9	19.77	19.72	19.62	19.56	19.86	20.97	21.19
10	26.39	26.64	26.20	26.43	26.52	26.44	26.36
11	36.69	36.62	25.97	25.92	25.83	25.89	25.67
12	76.67	76.77	33.58	33.60	33.36	33.55	31.77
13	47.59	47.60	41.36	41.39	42.22	41.84	40.53
14	48.24	48.25	46.58	46.60	46.37	46.98	53.27
15	43.35	43.37	79.47	79.49	80.51	79.74	211.52
16	72.51	72.55	110.96	110.99	110.78	111.46	103.43
17	55.97	56.00	58.99	58.97	59.45	59.19	56.92
18	12.97	12.97	18.98	18.98	19.37	19.16	20.33
19	29.79	29.91	30.67	30.75	30.84	30.53	29.95
20	25.34	25.33	23.47	23.45	23.39	23.68	23.05
21	20.76	20.73	19.33	19.32	19.86	19.33	19.74
22	36.29	36.33	37.75	37.74	37.44	37.67	37.23
23	105.16	105.19	71.23	71.28	71.37	71.74	72.58
24	62.22	62.17	89.46	89.40	88.92	89.06	89.62
25	64.59	62.60	70.42	70.40	70.88	71.31	71.15
26	12.47	12.44	25.04	25.04	25.73	25.93	25.53
27	97.23	97.29	25.30	25.33	25.83	25.93	25.91
28	19.49	19.53	11.22	11.23	12.45	11.11	14.24
29	25.34	25.55	25.30	25.59	25.43	22.21	22.24
30	14.91	14.07	14.95	14.20	15.14	20.76	20.69
1′	105.62		105.72				
2′	73.54		73.67				
3′	76.32		76.51				
4′	69.74		69.74				
5′	65.30		65.42				
CH_3CO	21.49	21.51			21.25 21.34		
$COCH_3$	170.17	170.27			170.84 171.04		

16. R=
17. R=OH

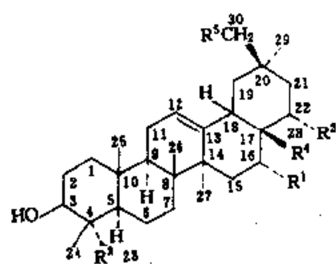
18. R^1=
R^2=OH

19. R^1=R^2=OH
20. R^1=R^2=OAc
21. R^1=O, R^2=OH
22. R^1=R^2=O

三、齐墩果烷类和熊果烷类三萜的^{13}C-NMR化学位移

表 21-45 齐墩果-12-烯三萜 23～29 的^{13}C-NMR化学位移数据[61]

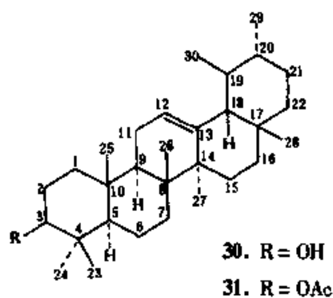
C \ 化合物	23	24	25	26	27	28	29
1	38.5(38.1)	38.1(37.7)	38.7(38.1)	38.0(37.7)	38.1(37.8)	39.0(38.3)	38.3(37.9)
2	27.1(23.6)	26.4(23.0)	27.0(23.4)	26.0(22.5)	26.0(22.5)	27.0(23.6)	26.0(23.0)
3	78.7(80.7)	76.4(74.3)	76.9(80.7)	71.8(73.2)	71.7(73.2)	78.8(80.7)	75.7(74.6)
4	38.7(37.5)	41.7(40.6)	38.7(37.7)	55.2(54.2)	55.2(54.2)	39.0(37.7)	41.7(40.6)
5	55.3(55.2)	49.7(47.7)	55.3(55.2)	48.0(47.7)	48.1(47.9)	55.6(55.2)	49.3(47.9)
6	18.3(18.2)	18.5(18.1)	18.5(18.3)	20.7(20.3)	20.7(20.4)	18.6(18.2)	18.3(18.0)
7	32.6(32.6)	32.4(32.3)	32.8(32.6)	32.3(32.2)	32.3(32.3)	32.8(32.5)	32.3(32.2)
8	39.3(39.5)	39.3(39.3)	39.3(39.2)	39.6(39.5)	39.7(39.7)	40.2(40.0)	39.7(39.8)
9	47.6(47.5)	47.5(47.7)	47.7(47.5)	47.5(47.5)	46.7(46.6)	47.9(47.5)	47.4(47.7)
10	37.0(36.9)	36.9(36.8)	37.2(36.9)	36.0(35.7)	35.9(35.8)	37.1(36.8)	36.8(36.7)
11	23.1(23.0)	23.3(23.0)	23.4(23.4)	23.0(22.8)	23.2(23.2)	23.8(23.6)	23.6(23.6)
12	122.1(122.1)	122.2(122.0)	122.8(122.7)	121.9(121.7)	122.2(123.0)	125.0(123.8)	122.1(122.6)
13	143.4(143.6)	143.6(143.6)	143.2(142.9)	143.6(143.6)	142.8(141.9)	143.2(141.9)	144.2(143.6)
14	41.6(41.6)	41.7(41.6)	41.7(41.4)	41.7(41.5)	41.4(41.0)	41.5(41.7)	41.7(41.6)
15	27.7(27.7)	27.7(27.7)	27.7(27.5)	27.6(27.6)	35.4(32.3)	25.3(25.0)	25.6(25.6)
16	23.4(23.6)	23.4(23.4)	23.4(23.4)	23.3(23.2)	74.7(76.0)	14.7(16.7)	21.9(22.2)
17	46.6(46.6)	46.7(46.6)	46.8(46.4)	46.5(46.5)	48.7(47.5)	43.0(40.1)	36.8(35.8)
18	41.3(41.3)	41.3(41.3)	40.3(40.7)	41.3(41.2)	40.5(40.3)	42.4(41.9)	42.5(42.6)
19	45.8(45.8)	45.9(45.8)	40.3(41.4)	45.8(45.7)	46.4(46.1)	46.9(44.1)	46.6(46.2)
20	30.6(30.6)	30.7(30.6)	35.2(33.7)	30.7(30.5)	30.3(30.3)	31.5(31.5)	30.9(30.9)
21	33.8(33.8)	33.9(33.8)	32.8(32.3)	33.8(33.7)	35.4(35.0)	42.4(38.9)	34.2(34.0)
22	32.3(32.4)	32.4(32.5)	32.1(31.7)	32.1(31.9)	30.3(30.9)	75.8(71.7)	30.9(31.4)
23	28.1(28.0)	71.3(65.3)	28.1(28.0)	207.0(204.0)	207.0(204.0)	78.2(28.0)	70.3(65.4)
24	15.6(16.8)	11.6(13.1)	15.7(16.7)	8.9(9.5)	9.0(9.5)	15.5(16.7)	11.6(13.1)
25	15.3(15.3)	15.7(15.8)	15.4(15.4)	15.5(15.5)	15.7(15.6)	15.6(15.5)	15.9(16.0)
26	16.8(16.8)	16.9(16.8)	16.9(16.7)	16.8(16.7)	16.9(16.8)	16.7(16.7)	16.7(16.7)
27	26.0(25.8)	26.0(25.8)	26.0(25.9)	26.0(25.8)	27.0(26.4)	26.4(26.2)	26.0(25.8)
28	177.9(177.8)	178.2(177.8)	178.5(177.4)	177.9(177.7)	177.2(175.6)	70.1(66.0)	69.1(70.7)
29	33.1(33.1)	33.1(33.1)	28.9(27.8)	33.1(33.0)	32.7(33.1)	33.4(33.0)	33.2(33.1)
30	23.6(23.6)	23.6(23.6)	65.8(67.7)	23.6(23.5)	24.6(24.2)	24.8(24.3)	23.6(23.6)
CO_2CH_3	51.3(51.4)	51.6(51.3)	50.6(51.2)	51.5(51.3)	51.9(52.0)		
COCH	(170.5)	(170.1)	(170.6)	(169.8)	(169.6)	(170.0)	(170.4)
		(170.5)	(170.9)		(170.0)	(170.7)	(170.7)
						(170.7)	(171.1)

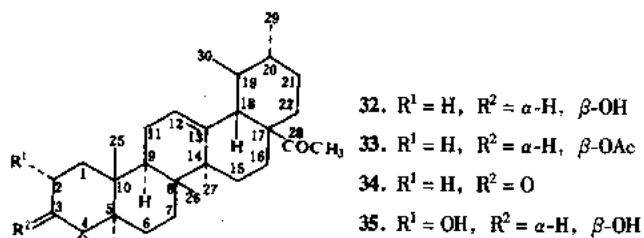


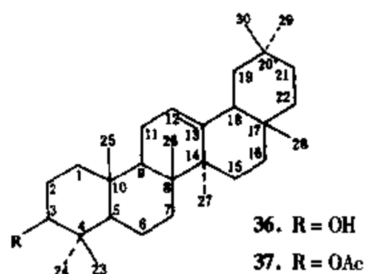
化合物	R^1	R^2	R^3	R^4	R^5
23	H	H	CH_3	CO_2CH_3	H
24	H	H	CH_2OH	CO_2CH_3	H
25	H	H	CH_3	CO_2CH_3	OH
26	H	H	CHO	CO_2CH_3	H
27	OH	H	CHO	CO_2CH_3	H
28	H	OH	CH_3	CH_2OH	H
29	H	H	CH_2OH	CH_2OH	H

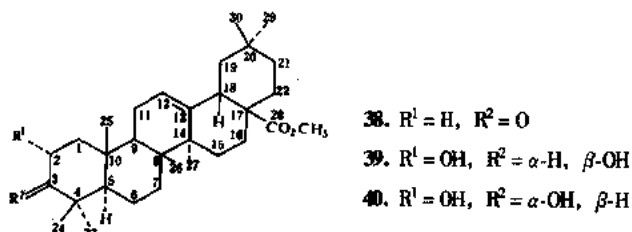
表 21-46 乌斯烯类和齐墩果烯类三萜 30～40 的 ^{13}C-NMR 化学位移数据[62,63]

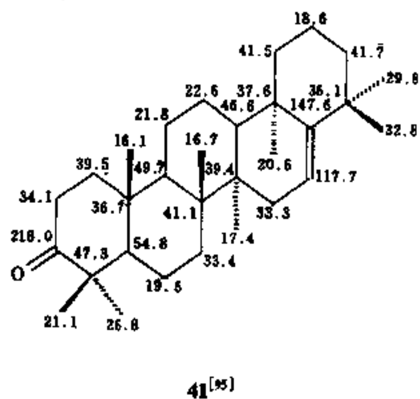
C \ 化合物	30	31	32	33	34	35	36	37	38	39	40
1	38.7	38.4	32.8	38.3	39.3	46.8	38.5	38.2	39.1	46.4	41.7
2	27.2	23.6	27.3	23.6	33.9	68.9	27.0	23.6	34.2	68.8	66.5
3	78.8	80.7	78.8	80.7	216.5	83.8	78.9	80.7	216.8	83.8	78.9
4	38.7	37.6	38.8	37.6	47.1	39.1	38.7	37.6	47.3	39.1	38.5
5	55.2	55.3	55.4	55.3	55.2	55.4	55.1	55.3	55.2	55.3	48.1
6	18.3	18.3	18.4	18.1	19.5	18.4	18.3	18.3	19.5	18.3	18.1
7	32.9	32.8	33.0	32.8	32.4	32.9	32.6	32.6	32.1	32.6	32.5
8	40.0	40.1	39.6	39.5	39.1	39.6	39.7	39.7	39.1	39.1	39.7
9	47.7	47.6	47.5	47.4	46.6	47.5	47.6	47.6	47.7	47.5	47.4
10	36.9	36.8	37.0	36.8	36.6	38.3	37.0	36.8	36.6	38.3	38.3
11	23.3	23.2	23.3	23.2	23.4	23.4	23.4	23.4	23.0	23.1	23.4
12	124.3	124.1	125.5	125.4	125.0	125.3	121.7	121.5	121.9	122.0	122.1
13	139.3	139.4	138.0	138.0	137.9	138.1	145.0	144.9	143.5	143.6	143.8
14	42.0	42.1	42.0	41.9	41.9	42.1	41.7	41.7	41.7	41.7	41.9
15	28.7	28.7	28.2	28.1	27.9	28.0	28.3	28.3	27.6	27.6	27.7
16	26.6	26.7	24.3	24.2	24.1	24.3	26.2	26.2	23.5	23.5	23.2
17	33.7	33.8	48.1	48.0	47.9	48.1	32.5	32.5	46.7	46.6	46.8
18	58.9	59.0	52.8	52.8	52.8	52.8	47.2	47.2	41.2	41.3	41.3
19	39.6	39.7	39.1	38.9	38.8	39.1	46.8	46.8	45.7	45.8	46.0
20	39.6	39.7	38.8	38.9	38.8	38.9	31.1	31.1	30.5	30.7	30.7
21	31.2	31.3	30.7	30.7	30.5	30.7	34.8	34.8	33.7	33.8	34.0
22	41.5	41.5	36.7	36.6	36.6	36.7	37.2	37.1	32.1	32.3	32.5
23	28.1	28.1	28.2	28.1	26.5	28.7	28.1	28.1	26.4	28.6	28.5
24	15.6	16.8	15.5	16.9	21.3	17.0	15.5	16.8	21.3	16.8	21.9
25	15.6	15.7	15.7	15.5	15.1	17.0	15.5	15.7	14.8	16.8	16.4
26	16.8	16.8	16.9	16.9	16.8	17.0	16.8	16.8	16.7	16.8	17.0
27	23.3	23.2	23.6	23.6	23.4	23.7	26.0	26.0	25.7	26.0	26.2
28	28.1	28.1	177.7	177.6	177.3	177.9	27.3	27.0	177.7	178.0	178.1
29	17.4	17.5	16.9	17.1	16.8	17.0	33.2	33.4	33.0	33.1	33.2
30	21.3	21.4	21.2	21.2	21.1	21.2	23.6	23.6	23.5	23.5	23.6
CO_2CH_3			51.4	51.3	51.2	51.5			51.3	51.5	51.5
$OCOCH_3$		21.2		21.2							
$OCOCH_3$		170.4		170.5							



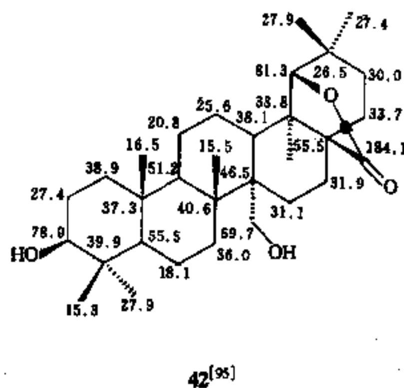




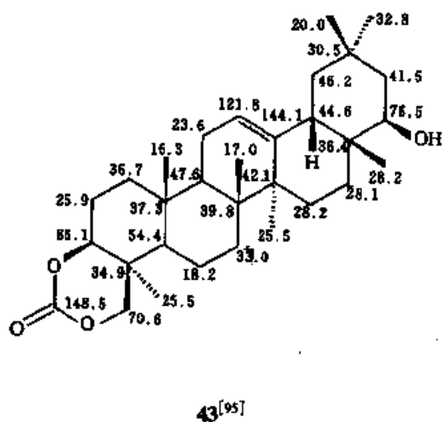




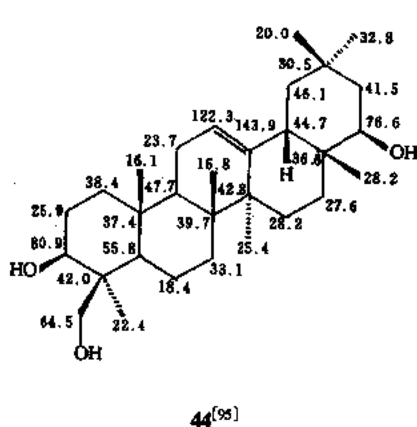
41[95]



42[95]



43[95]

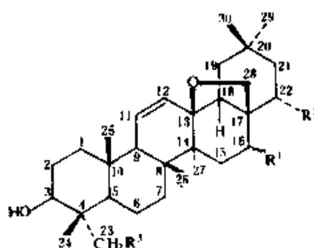


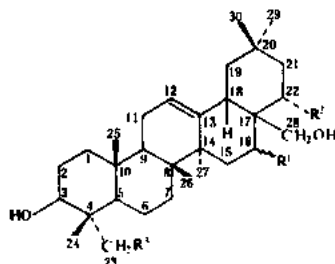
44[95]

四、柴胡皂甙类三萜的¹³C-NMR化学位移

表 21-47 柴胡皂甙元三萜 45～53 的¹³C-NMR 化学位移数据[64]

C \ 化合物	45	46	47	48	49	50	51	52	53
1	38.0	38.0	38.4	38.2	38.2	38.4	38.8	38.5	38.5
2	26.2	26.1	26.9	26.1	26.2	26.4	26.9	26.7	26.3
3	75.9	75.6	78.7	75.4	75.2	76.7	78.9	76.5	76.0
4	41.9	42.0	39.0	42.0	42.2	41.9	38.8	42.0	41.8
5	49.3	49.2	54.9	49.1	49.0	49.9	55.3	49.9	49.3
6	17.7	17.7	17.9	17.8	17.8	18.5	18.4	18.7	18.4
7	31.1	31.1	31.5	31.3	31.2	32.6	32.6	32.6	32.6
8	41.6	41.4	41.8	41.9	41.8	40.0	39.9	40.0	39.8
9	53.3	52.5	52.7	52.7	52.8	47.0	46.8	47.0	46.7
10	36.3	36.3	36.4	36.3	36.4	36.9	36.9	37.0	36.0
11	132.5	132.6	132.9	133.0	133.2	23.4	23.6	23.7	23.5
12	130.7	130.5	129.7	129.7	130.3	122.6	122.6	122.7	122.9
13	85.2	85.1	84.1	84.3	85.5	143.1	142.8	143.0	142.7
14	43.9	43.0	45.4	45.5	43.8	41.6	43.7	43.9	41.8
15	25.7	34.7	35.1	35.0	34.3	34.7	35.8	36.2	33.4
16	25.3	77.3	64.7	64.6	70.5	74.9	67.7	68.0	67.9
17	41.6	44.9	46.3	46.4	47.5	40.6	40.0	40.4	43.9
18	51.1	50.6	51.7	51.9	50.4	42.8	44.7	44.9	42.4
19	37.2	38.0	37.5	37.5	37.4	47.0	46.7	47.0	47.2
20	31.7	31.7	31.5	31.6	33.2	30.4	30.8	30.9	31.4
21	34.9	36.5	34.3	34.3	45.7	35.4	33.6	33.7	44.8
22	30.9	30.5	25.1	25.2	74.3	26.8	26.2	26.2	75.5
23	70.7	70.3	27.8	70.0	69.6	71.9	28.1	71.7	70.8
24	11.1	11.1	15.0	11.2	11.3	11.5	15.6	11.6	11.7
25	18.2	18.3	17.9	18.3	18.4	16.1	15.6	16.0	16.0
26	19.3	19.0	19.5	19.5	19.1	17.2	16.7	16.9	16.2
27	19.3	17.9	20.7	20.7	18.1	27.3	26.9	26.9	27.0
28	77.1	77.3	72.4	72.5	76.9	70.8	70.9	71.1	71.1
29	33.7	33.4	33.6	33.6	33.2	32.8	33.2	33.1	33.2
30	23.6	24.2	23.7	23.8	25.2	25.5	23.9	24.0	24.9





45. R^1 = H, R^2 = H, R^3 = H

46. R^1 = α-OH, R^2 = H, R^3 = OH

47. R^1 = β-OH, R^2 = H, R^3 = H

48. R^1 = β-OH, R^2 = H, R^3 = OH

49. R^1 = α-OH, R^2 = OH, R^3 = OH

50. R^1 = α-OH, R^2 = H, R^3 = OH

51. R^1 = β-OH, R^2 = H, R^3 = H

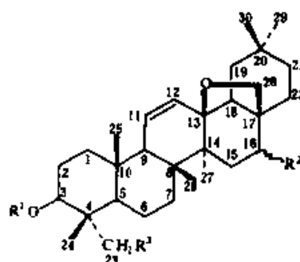
52. R^1 = β-OH, R^2 = H, R^3 = OH

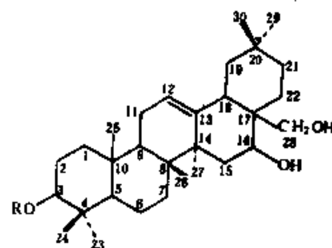
53. R^1 = α-OH, R^2 = OH, R^3 = OH

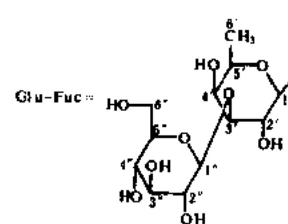
表 21-48　柴胡皂甙类三萜 54～57 的^{13}C-NMR 化学位移数据[65]①

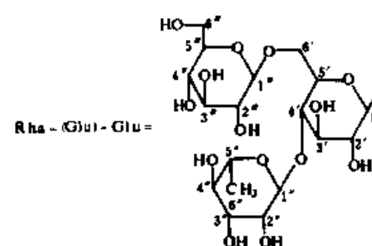
C \ 化合物	54	55	56	57	C \ 化合物	54	55	56	57
1	38.8	38.9	38.8	39.1	25	18.7	18.6	18.1	15.7
2	25.8	25.7	26.4	26.4	26	19.4	19.8	19.8	17.1
3	82.5	82.5	89.2	89.3	27	18.1	20.8	20.8	27.1
4	43.8	43.5	39.7	39.5	28	77.8	72.9	72.9	69.3
5	48.1	48.0	55.7	56.1	29	33.7	33.7	33.7	33.3
6	17.8	17.8	18.1	18.7	30	24.5	23.9	23.9	24.3
7	31.8	31.9	32.2	33.4	1′	105.4	105.3	106.1	106.1
8	42.1	42.4	42.4	40.4	2′	71.1	71.7	75.2	75.2
9	53.2	53.2	53.1	47.4	3′	85.1	85.0	76.8	76.9
10	36.6	36.6	36.6	37.1	4′	71.9	71.8	80.2	80.2
11	131.9	132.0	132.0	24.0	5′	70.9	70.8	75.2	75.5
12	131.9	131.0	131.1	122.8	6′	16.9	16.9	69.2	69.3
13	85.1	84.0	84.0	144.0	1″	105.8	105.7	102.6	102.6
14	43.7	46.0	45.9	44.1	2″	75.5	75.4	72.6	72.6
15	35.7	36.2	36.2	36.8	3″	78.1	78.0	72.2	72.3
16	77.5	64.4	64.4	67.2	4″	71.9	71.8	73.8	73.8
17	45.5	46.9	47.0	41.1	5″	78.1	78.0	70.5	70.5
18	51.5	52.4	52.3	44.9	6″	63.0	62.9	18.1	18.2
19	38.7	38.2	38.1	47.4	1‴			104.8	104.8
20	31.8	31.6	31.6	31.0	2‴			74.7	74.7
21	37.0	35.0	34.9	34.4	3‴			78.2	78.3
22	31.2	25.6	25.7	26.4	4‴			71.8	71.9
23	65.2	65.1	28.1	28.4	5‴			77.9	78.0
24	12.8	12.7	16.3	17.0	6‴			62.9	62.9

① 在 C_5D_5N 中测定。







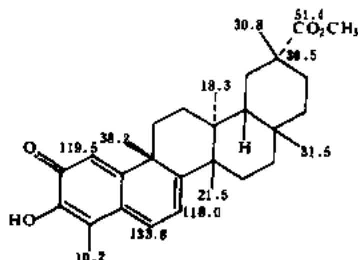


54. R^1 = Glu-Fuc, R^2 = α-OH, R^3 = OH

55. R^1 = Glu-Fuc, R^2 = β-OH, R^3 = OH

56. R^1 = Rha-(Glu)-Glu, R^2 = β-OH, R^3 = H

57. R = Rham-(Glu)-Glu



58[66]. CH_2: 28.6, 29.6, 29.8, 30.4, 33.5, 34.8, 36.3

C: 38.3, 39.3, 40.3, 44.9

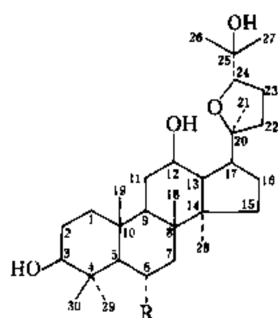
>C= : 117.1, 127.2, 146.0, 164.0, 169.8, 178.1, 178.4

五、呋喃三萜类^{13}C-NMR化学位移

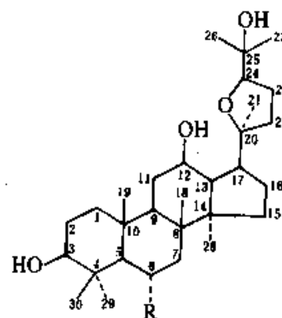
表 21-49 呋喃三萜 59～63 的^{13}C-NMR化学位移数据[67]①

C \ 化合物	59	60	61	62	63	C \ 化合物	59	60	61	62	63
1	39.4	39.5	39.4	39.7	39.6	25	70.2	70.0	70.2	70.1	70.0
2	28.0	28.1	27.5	27.8	27.9	26	27.1	26.6	27.0	26.7	26.6
3	78.3	78.4	78.1	78.0	78.1	27	27.6	29.0	27.5	29.0	29.0
4	40.3	40.3	39.8	40.3	40.3	28	31.8	31.9	31.9	32.4	31.7
5	61.8	61.9	60.7	61.5	61.4	29	16.4	16.5	16.8	16.8	16.7
6	67.6	67.7	73.9	79.9	79.5	30	18.2	18.1	18.0	17.9	17.9
7	47.4	47.5	45.8	45.0	44.9	6-glu 1				103.6	103.5
8	41.0	41.2	40.9	41.2	41.1	2				79.9	79.9
9	50.4	50.2	49.9	50.4	50.3	3				78.6	78.8
10	39.4	39.3	39.4	39.7	39.6	4				71.7	71.3
11	32.3	32.2	31.8	32.4	32.6	5				79.9	80.4
12	71.1	70.8	71.0	71.0	70.9	6				63.0	63.0
13	48.3	49.1	48.1	49.2	49.2	6-glu 1′				103.9	
14	52.0	52.2	52.0	52.3	52.3	2′				76.0	
15	31.7	32.6	31.6	32.4	32.6	3′				78.6	
16	25.4	25.8	25.3	25.8	25.8	4′				72.4	
17	49.3	49.5	49.2	49.5	49.5	5′				79.9	
18	17.7	17.8	17.7	17.9	17.9	6′				63.5	
19	17.4	17.2	17.4	17.3	17.2	6-xyl 1					104.9
20	86.6	87.0	86.5	87.1	87.1	2					75.9
21	26.9	26.9	26.8	27.1	27.0	3					78.8
22	32.8	32.6	32.6	32.4	32.6	4					71.7
23	28.6	28.7	28.7	29.0	28.7	5					67.3
24	85.6	88.4	85.7	88.4	88.4						

① 在 C_5D_5N 中测定。



60. R＝—OH
62. R＝—O-glu$^{2-1}$glu
63. R＝—O-glu$^{2-1}$xyl



59. R＝—OH
61. R＝—O-glu$^{2-1}$rha

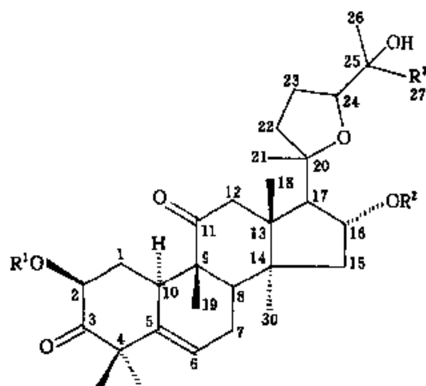
表 21-50 呋喃三萜甙 64～72 的^{13}C-NMR谱化学位移[96]

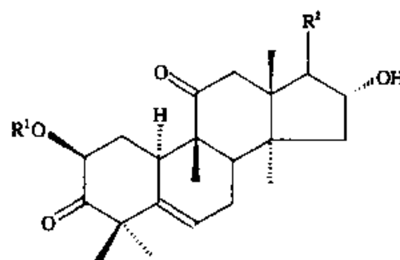
C \ 化合物	64①	65	66	67	68①	69①	70①	71①	72①
1	35.8	35.9	33.7	36.0	28.3	35.9	28.3	35.9	28.3
2	79.4	79.7	75.9	71.6	76.9	79.7	76.8	79.7	76.9
3	213.4	213.3	208.6	212.2	76.8	213.3	77.0	213.4	76.8
4	52.4	49.2	51.2	50.2	42.3	52.4	42.3	52.4	42.4
5	141.7	141.7	139.9	140.5	139.7	141.7	139.8	141.7	139.8
6	121.4	121.4	120.2	120.4	121.1	121.4	121.0	121.4	121.1
7	24.9	24.9	23.8	24.0	24.9	24.9	24.9	24.9	24.9

续表

化合物 / C	64①	65	66	67	68①	69①	70①	71①	72①
8	44.2	44.2	42.4	42.9	44.7	44.3	44.7	44.2	44.6
9	49.8	49.3	48.7	48.7	50.2	49.8	50.1	50.1	50.2
10	35.1	35.1	34.3	33.8	35.0	35.1	35.0	35.1	35.0
11	216.2	215.8	212.1	213.0	216.8	216.2	216.4	216.1	216.6
12	49.8	49.9	48.2	48.2	49.5	49.9	49.8	49.9	49.9
13	49.3	52.4	50.2	49.8	49.2	49.3	49.2	49.3	49.2
14	51.8	51.8	47.5	47.8	51.9	51.8	51.9	51.5	51.6
15	47.0	46.6	44.1	44.7	47.1	47.1	47.2	46.6	46.7
16	73.6	71.9	75.7	73.0	73.7	73.5	73.5	73.1	73.2
17	62.0	60.3	57.5	62.3	62.0	61.9	61.9	60.2	60.2
18	20.6	20.7	19.8	20.0	20.6	20.6	20.6	20.5	20.4
19	20.1	20.1	20.1	20.5	20.2	20.1	20.3	20.1	20.2
20	86.2	81.1	84.1	86.0	86.2	86.4	86.4	75.8	75.8
21	28.6	25.6	28.5	26.0	26.4	28.5	28.5	26.4	26.4
22	28.6	205.4	37.7	38.9	38.9	38.6	38.6	45.1	45.1
23	26.4	122.7	24.6	26.1	26.4	25.7	26.7	23.3	23.3
24	89.3	151.5	88.3	86.7	89.2	85.8	85.8	129.1	129.1
25	71.9	80.3	70.1	70.1	71.9	73.6	73.5	135.5	135.5
26	25.6	26.8	27.9	27.9	25.6	69.3	69.3	61.5	61.5
27	26.5	26.5	24.1	24.4	28.6	20.4	20.6	21.5	21.6
28	29.4	29.4	28.4	29.4	27.4	29.4	27.5	29.4	27.4
29	21.8	21.8	21.5	21.3	26.1	21.8	26.3	21.8	26.1
30	19.2	19.5	18.3	19.0	19.3	19.2	19.3	19.3	19.4
1′	104.3	104.4	99.5		102.0	104.3	101.9	104.3	102.0
2′	75.5	75.5	71.4		75.1	75.5	75.2	75.4	75.2
3′	78.2	78.2	72.7		78.1	78.3	78.2	78.2	78.1
4′	71.5	71.5	68.5		71.6	71.5	71.7	71.5	71.7
5′	78.0	78.0	71.7		77.9	78.0	77.9	77.9	77.9
6′	62.9	63.0	61.8		62.9	62.9	62.8	62.9	62.9
Me		21.9	21.5						
			20.8						
			20.8						
			20.6						
			20.6						
CO		169.3	169.3						
			169.7						
			170.1						
			170.5						
			170.7						

① 在 CD_3OD 中测定。





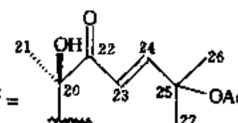
64. $R^1 = \beta$-D-Glc，$R^2 = H$，$R^3 = CH_3$

66. $R^1 = \beta$-D-GlcAc$_4$，$R^2 = Ac$，$R^3 = CH_3$

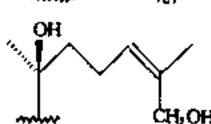
67. $R^1 = R^2 = H$，$R^3 = CH_3$

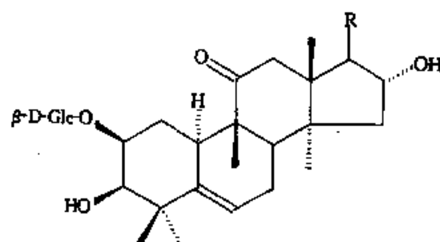
69. $R^1 = \beta$-D-Glc，$R^2 = H$，$R^3 = CH_2OH$

65. $R^1 = \beta$-D-Glc，$R^2 =$

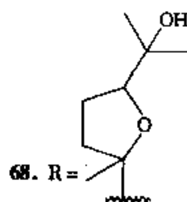


71. $R^1 = \beta$-D-Glc，$R^2 =$

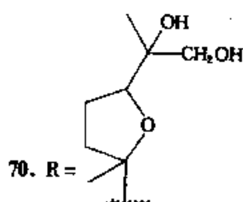




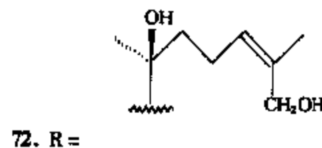
68. R =



70. R =



72. R =



六、何帕烷类三萜的^{13}C-NMR 化学位移

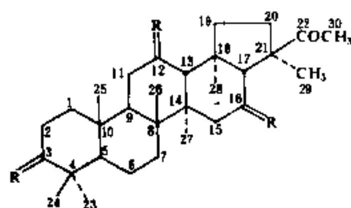
表 21-51　何帕烷类三萜 72～86 的^{13}C-NMR 化学位移数据[68]①

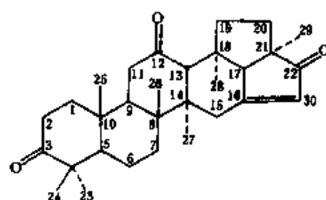
C \ 化合物	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
1	38.5	37.9	38.9	38.3	38.6	37.2	37.9	40.7	38.5	38.7	39.5	38.8	39.7	38.6	40.1
2	27.2	23.3	33.5	33.5	27.0	22.6	23.0	33.9	23.6	27.4	34.0	27.3	33.9	23.6	18.3
3	76.9	80.2	215.9	216.0	77.2	79.7	80.2	213.8	79.6	78.8	217.9	78.3	218.3	80.8	40.9
4	38.5	37.5	47.0	47.0	39.0	38.8	39.1	48.7	39.2	38.8	47.2	38.8	47.1	37.7	33.1
5	54.8	54.8	54.5	54.8	59.8	57.4	57.8	65.0	145.6	55.2	54.8	55.4	54.8	55.5	58.2
6	18.2	18.4	19.3	19.0	66.6	70.2	70.6	210.2	120.2	18.3	19.6	18.2	19.6	18.0	71.6
7	33.0	32.7	31.3	31.4	42.6	39.2	39.5	48.7	33.8	34.2	33.5	34.5	33.9	33.3	40.7
8	41.0	41.3	41.4	41.1	42.3	42.3	42.6	43.6	40.7	40.8	40.7	40.6	40.4	40.7	42.7

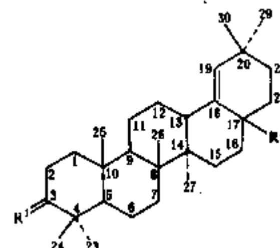
续表

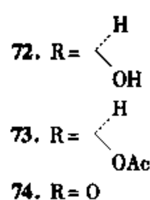
化合物 / C	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
9	48.3	47.6	49.2	47.5	49.0	48.7	49.0	50.0	45.9	50.4	49.7	51.1	50.3	51.0	49.1
10	36.5	36.7	36.5	36.5	38.6	37.1	37.4	40.7	37.0	37.1	36.8	37.1	36.8	37.0	39.4
11	32.0	27.4	38.3	38.2	20.6	20.3	20.6	21.3	20.5	20.9	21.4	20.9	21.4	21.1	20.7
12	64.2	69.5	208.3	210.1	22.9	22.5	22.8	21.8	22.1	25.1	25.1	25.6	25.9	26.0	23.3
13	54.6	51.9	63.1	64.0	47.1	47.0	47.2	46.1	48.2	38.0	38.1	41.2	41.3	38.3	48.5
14	44.8	45.4	50.4	45.9	43.3	43.4	44.0	52.5	43.5	42.9	42.8	42.5	42.4	43.2	44.0
15	44.8	39.8	49.2	36.7	45.2	40.6	41.0	50.0	40.1	27.4	27.4	29.3	29.3	27.4	41.4
16	67.5	71.4	208.9	179.4	66.9	73.7	73.6	212.4	74.2	35.5	35.4	33.5	33.7	37.3	73.1
17	62.9	58.6	61.8	61.2	57.4	54.2	54.5	63.1	54.6	42.9	42.9	48.1	48.1	34.2	56.8
18	46.1	46.1	49.7	47.0	46.3	47.7	46.4	51.4	48.3	48.2	48.2	136.9	136.7	142.5	46.5
19	44.5	43.8	40.7	43.1	39.6	39.2	40.0	41.1	39.7	47.9	47.8	132.3	132.9	129.6	43.3
20	36.8	36.9	35.8	34.8	25.8	26.3	20.7	23.2	26.8	150.6	150.5	32.0	31.9	32.2	27.7
21	52.3	52.2	54.1	55.3	52.0	51.5	44.5	50.2	51.8	29.8	29.8	33.5	33.4	34.5	51.6
22	213.8	212.3	211.2	213.6	70.5	71.1	28.0	71.5	71.6	39.9	39.9	33.5	33.4	37.6	72.9
23	28.2	27.7	26.1	26.1	30.1	29.8	30.2	25.5	27.7	28.0	26.6	27.9	26.8	27.8	36.2
24	15.8	16.2	22.5	23.5	16.2	16.2	16.5	24.3	24.0	15.4	21.0	16.6	20.9	16.6	22.0
25	15.7	15.4	14.7	14.4	15.8	15.7	15.8	16.2	23.1	16.1	15.8	15.4	15.8	16.0	16.9
26	16.7	16.6	16.7	15.7	16.8	16.4	16.7	16.2	16.3	15.9	15.9	15.9	16.4	16.4	18.0
27	17.3	17.2	18.3	21.0	17.6	17.1	17.6	17.4	17.7	14.5	14.4	14.9	14.8	14.4	18.0
28	18.6	17.9	20.7	23.0	18.1	17.5	17.9	18.1	17.7	18.0	18.0	176.8	176.8	25.1	17.0
29	25.9	25.0	25.0	24.0	31.2	29.1	22.3	30.1	29.4	109.2	109.2	30.3	30.3	31.2	27.4
30	20.2	19.8	20.9	127.6	22.9	23.3	14.8	24.3	23.6	19.3	19.3	29.1	29.1	29.1	30.3
3-$OCOCH_3$		170.4				170.1	170.6		170.5					170.7	
		21.5				21.4	21.7		21.4					21.0	
6, 12-$OCOCH_3$		169.9				168.9	170.0								170.0
		20.6				20.6	21.0								21.9
16-$OCOCH_3$		170.0				169.5	170.5		169.3						170.0
		20.9				21.0	21.1		21.1						21.9
OCH_3												51.8	51.8		

① 在$(CD_3)_2SO$中测定。







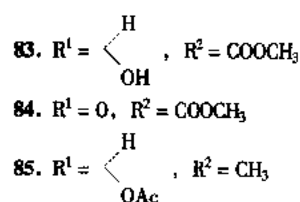


72. R = H / OH

73. R = H / OAc

74. R = O

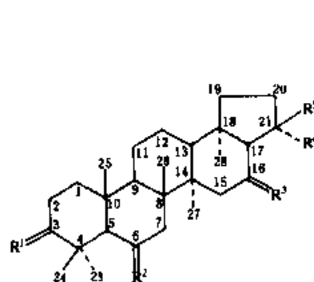
75

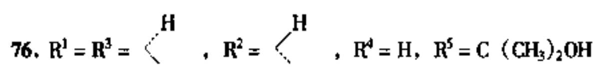


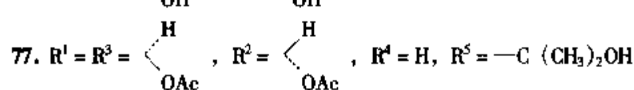
83. R^1 = H / OH, $R^2 = COOCH_3$

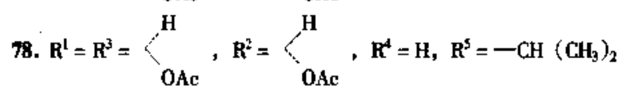
84. R^1 = O, $R^2 = COOCH_3$

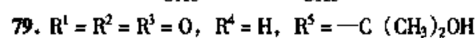
85. R^1 = H / OAc, $R^2 = CH_3$

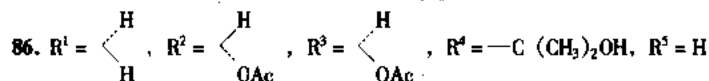


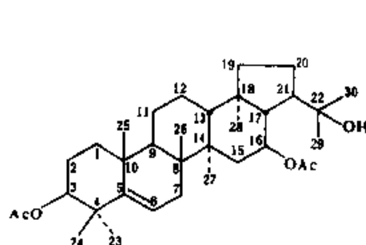


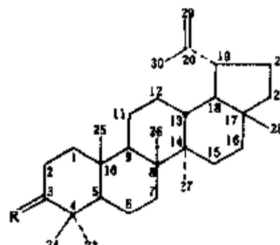


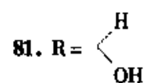












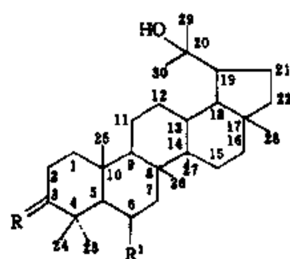


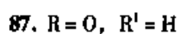
80

七、羽扇豆烷型三萜的^{13}C-NMR化学位移

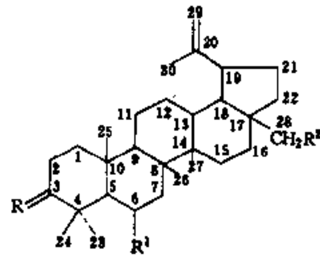
表 21-52　羽扇豆烷型三萜 87～92 的^{13}C-NMR 化学位移数据

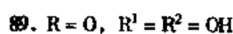
C \ 化合物	87	88	89	90	91	92	C \ 化合物	87	88	89	90	91	92
1	39.6	42.5	42.2	43.0	39.6	43.4	16	35.6	35.6	36.8	35.5	35.6	35.4
2	34.6	34.4	34.5	34.5	34.1	33.8	17	44.6	44.6	47.8	43.2	42.9	43.9
3	217.8	216.8	216.6	216.7	217.9	214.6	18	48.3	48.5	47.8	48.3	48.3	48.1
4	47.2	48.9	48.9	49.0	47.3	48.5	19	49.7	50.1	47.9	48.0	47.9	50.1
5	54.9	56.6	57.0	56.6	55.0	65.1	20	73.4	73.4	150.3	150.8	150.7	73.3
6	19.7	69.7	69.6	69.7	19.6	211.6	21	29.7	29.1	29.8	29.8	29.9	28.2
7	33.9	42.1	42.2	42.2	33.6	52.2	22	40.2	40.2	29.2	39.9	40.0	39.9
8	41.4	40.7	40.2	40.0	40.8	41.0	23	26.7	24.9	25.1	25.0	26.6	24.1
9	50.0	50.6	50.7	50.7	49.8	50.2	24	21.0	23.7	23.8	23.7	21.0	21.9
10	36.8	36.8	36.5	36.8	36.9	46.2	25	16.0	17.5	17.0	17.0	15.8	16.4
11	22.0	21.8	21.2	21.3	21.5	21.7	26	16.0	17.0	17.1	17.1	15.4	16.2
12	28.7	28.7	25.4	25.2	25.2	28.6	27	14.8	15.2	15.1	14.8	14.4	15.2
13	37.7	36.8	34.0	37.2	38.2	37.3	28	19.2	19.2	60.5	18.0	18.0	19.2
14	43.6	43.9	43.1	42.2	42.9	44.4	29	31.6	31.7	109.8	109.4	109.2	32.0
15	27.6	27.7	27.2	27.5	27.4	27.6	30	24.8	25.2	19.5	19.3	19.3	24.5

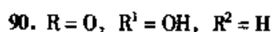


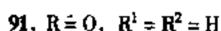


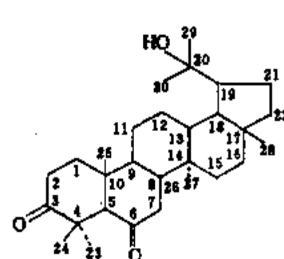












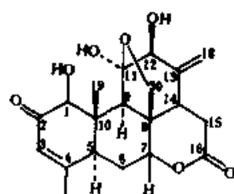


第六节　其他萜类化合物的^{13}C-NMR 化学位移

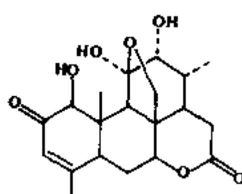
一、苦木苦素类化合物的^{13}C-NMR 化学位移

表 21-53　苦木苦素类化合物 1～6 的^{13}C-NMR 化学位移数据[69]

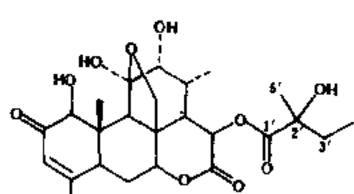
C \ 化合物	1	2	3	4	5	6	C \ 化合物	1	2	3	4	5	6
1	85.2	82.5	82.6	82.6	48.7	47.8	16	169.1	169.4	166.8	167.1	167.0	168.0
2	197.2	197.1	196.8	71.3	192.9	193.0	18	119.7	12.5	14.8	14.8	169.9	168.0
3	125.0	124.7	124.8	125.7	144.1	144.3	19	9.5	9.4	9.9	10.1	15.0	15.2
4	162.5	162.3	162.5	133.8	128.3	129.4	30	71.2	70.1	70.0	70.1	72.3	73.6
5	43.3	43.1	43.9	40.1	39.9	42.1	$4CH_3$	22.2	22.1	22.1	20.9	13.3	13.1
6	25.1	25.0	24.7	24.9	28.7	29.1	1′			174.4	174.4	168.7	165.9
7	77.7	77.6	77.4	77.9	82.8	83.2	2′			73.9	73.9	20.4	111.5
8	44.5	44.9	46.8	76.7	44.7	45.5	3′			32.5	32.6		171.3
9	46.1	41.1	41.1	40.9	40.4	41.6	4′			7.6	7.7		73.6
10	44.5	44.3	44.5	44.1	40.9	41.1	5′			24.7	24.9		27.9
11	108.9	108.9	108.9	109.1	71.4	71.2	6′						27.9
12	79.1	77.9	78.4	78.5	74.7	75.4	7′					52.3	15.2
13	146.6	30.4	31.4	31.4	81.4	81.6	OCH_3					52.3	52.7
14	41.1	41.1	44.5	44.6	48.7	49.7							
15	34.3	29.4	69.8	69.5	67.3	66.7							



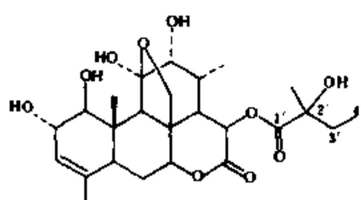
1



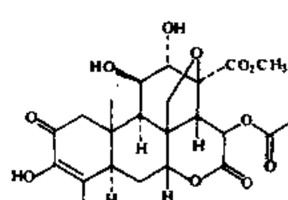
2



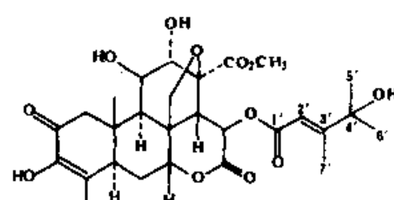
3



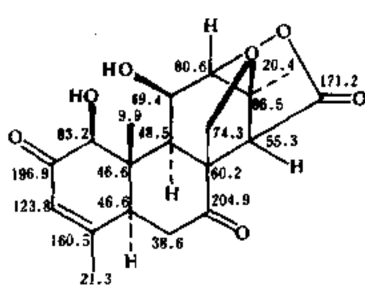
4



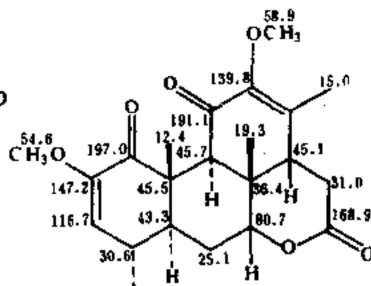
5



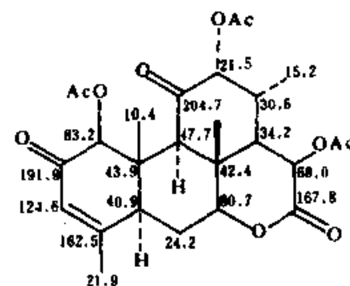
6



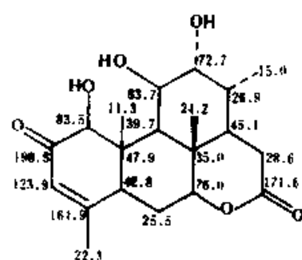
7[69]

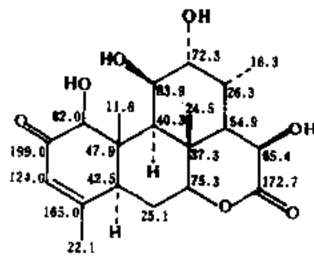


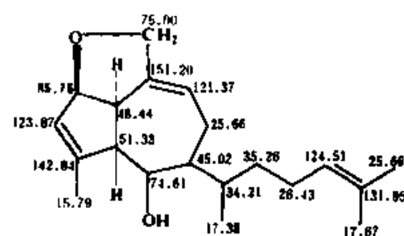
8[69]

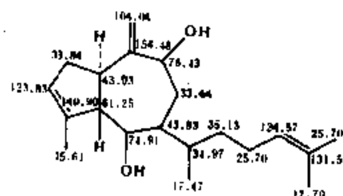


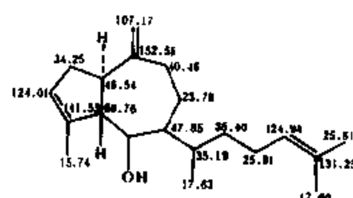
9[69]


10[69]


11[69]


12[69]

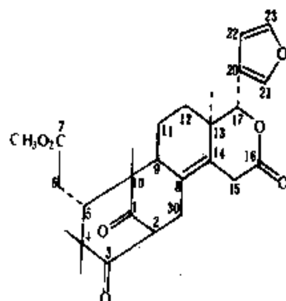

13[70]

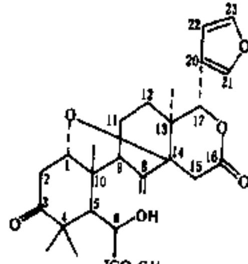

14[70]

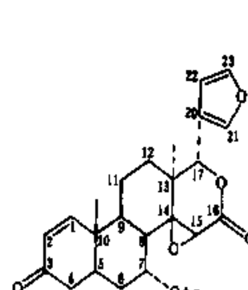
二、柠檬苦素类化合物的^{13}C-NMR 化学位移

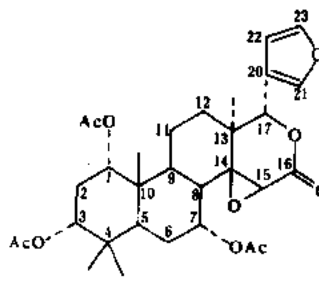
表 21-54 柠檬苦素类化合物 15～18 的^{13}C-NMR 化学位移数据[71]

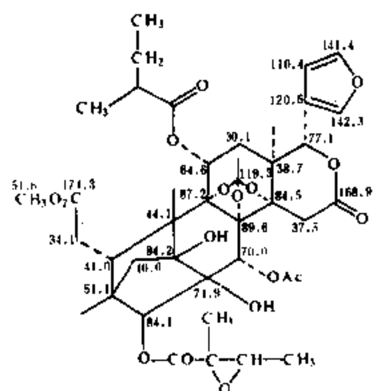
C \ 化合物	15	16	17	18	C \ 化合物	15	16	17	18
1	202.7	79.2	157.0	72.3	20	120.4	121.6	120.5	120.5
2	58.0	40.1	125.9	25.6	21	142.7	143.3	143.0	143.0
3	210.9	212.2	203.8	75.9	22	109.8	110.7	109.8	109.9
4	49.4	49.8	44.0	35.9	23	141.5	141.3	141.4	141.4
5	50.5	51.9	39.5	37.0	30	36.4	112.3		
6	32.3	73.3	14.9	22.3	OCH_3	52.1	54.2		
7	173.5	177.1	73.2	73.8	CH_3	21.9	25.9	27.2	27.4
8	133.8	146.6	42.6	42.2		17.8	24.9	26.0	21.6
9	40.2	48.5	46.0	36.3		17.8	24.5	23.3	21.3
10	54.3	45.7	40.0	40.7		17.4	15.0	21.7	21.1
11	18.6	25.1	17.7	14.4				21.0	21.1
12	28.8	29.7	18.3	26.1				19.7	18.3
13	37.8	42.4	38.7	38.8					17.3
14	125.3	81.3	69.8	69.7					16.4
15	32.9	34.5	56.9	56.4	CO			169.8	169.9
16	169.7	170.5	167.4	167.6					169.7
17	80.6	80.3	78.2	78.4					169.6


15

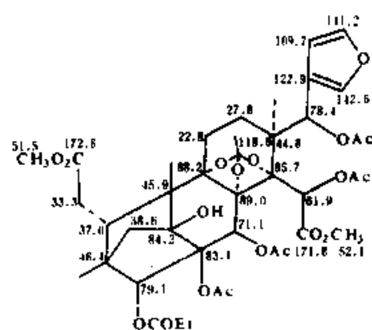

16


17


18

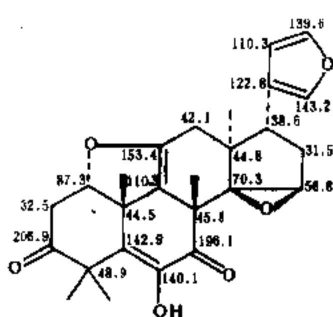


19[71]

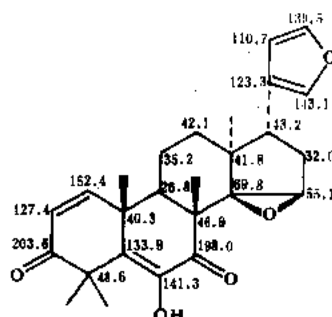


20[71]

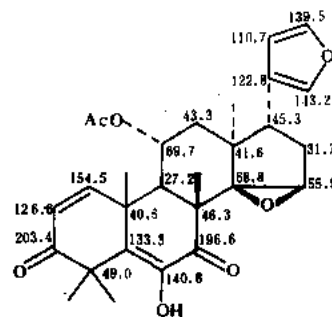
三、楝烷类化合物的^{13}C-NMR 化学位移



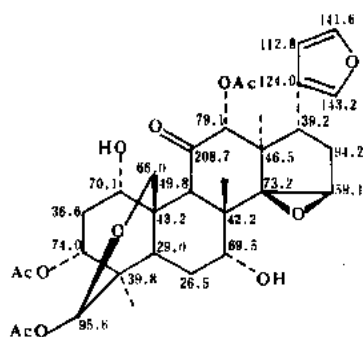
21[72]
CH_3:29.2,25.5,21.1,20.6,17.6



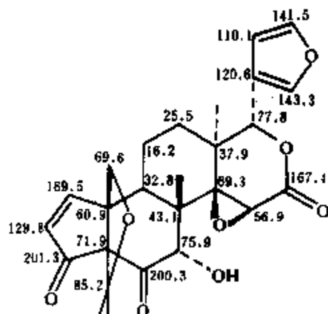
22[72]
CH_3:23.9,23.1,21.3,
20.2,19.5



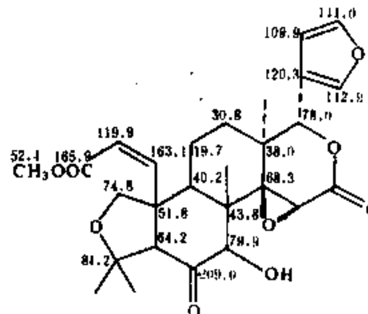
23[72]
CH_3:24.2,22.8,21.9,21.4,
21.1,19.7



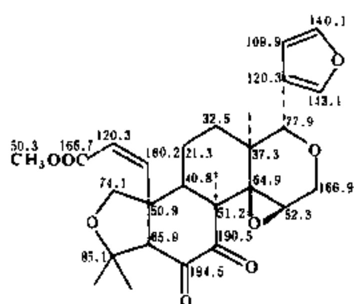
24[73]
CH_3:20.7,19.2,15.7



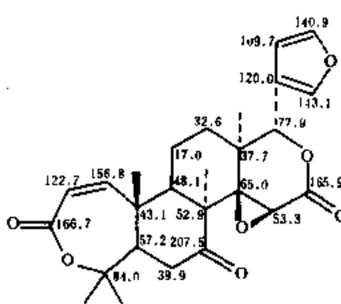
25[74]
CH_3:28.8,25.1,17.7,15.5



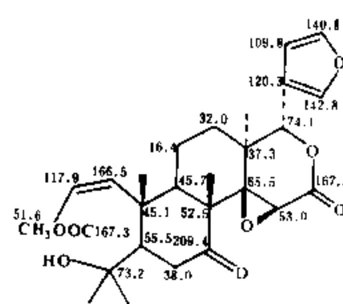
26[74]
CH_3:30.8,25.0,20.3,12.3



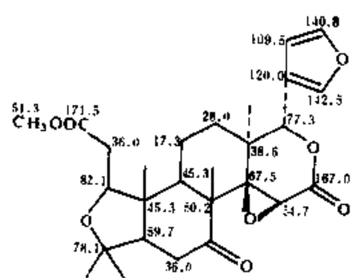
27[74]
CH_3:29.0,25.3,19.7,10.0



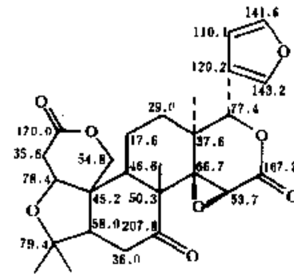
28[74]
CH_3:32.0,26.7,21.0,
19.4,16.4



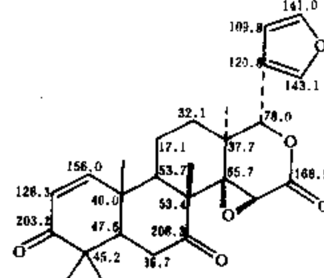
29[74]
CH_3:32.6,29.4,20.7,
20.3,19.4



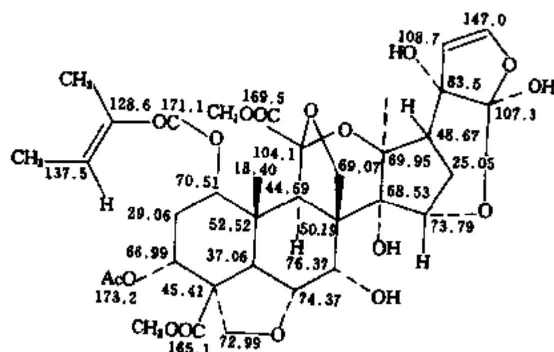
30[74]
CH_3:29.2,22.9,19.5,
18.4,11.8



31[74]
CH_3:29.5,21.3,19.7,17.1

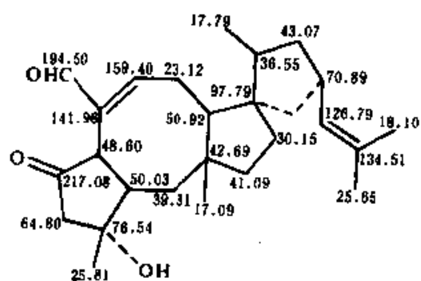


32[74]
CH_3:22.0,20.9,20.7,19.7,17.4

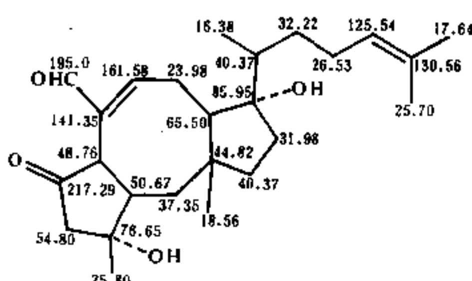


33[84]
CH_3: 53.52, 52.72, 20.88, 18.40, 14.29, 11.54

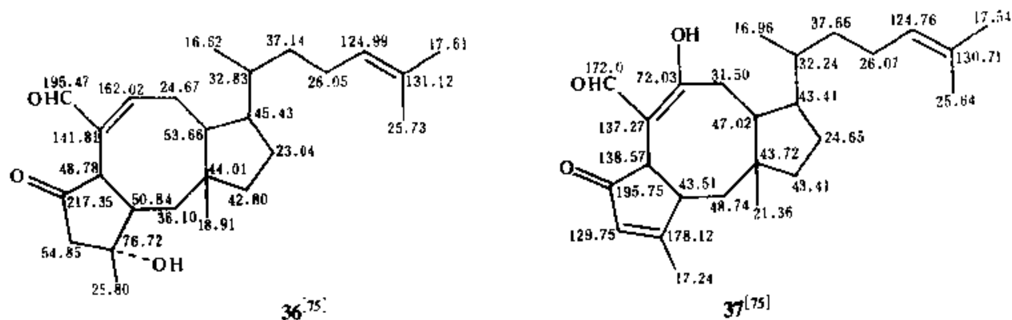
四、二倍半萜的^{13}C-NMR 化学位移



34[75]



35[75]

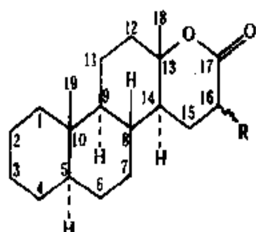


36[75]　　　　37[75]

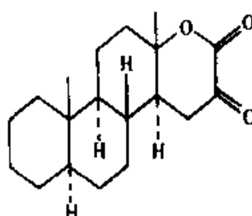
五、多环内酯的^{13}C-NMR化学位移

表 21-55　多环内酯 38～44 的^{13}C-NMR 化学位移数据[76]

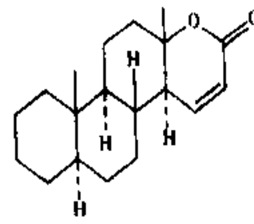
C \ 化合物	38	39	40	41	42	43	44
1	38.4	38.4	38.5	38.4	38.3	38.5	38.4
2	22.0	22.0	21.9	21.9	21.9	21.9	22.0
3	26.6	26.7	26.6	26.6	26.5	26.5	26.6
4	28.7	28.7	28.5	28.5	28.6	28.4	28.7
5	46.6	46.3	46.3	46.3	46.3	46.3	46.7
6	28.7	28.5	28.5	28.5	28.6	28.6	28.5
7	30.6	30.6	30.5	30.7	30.7	30.2	30.4
8	37.9	37.2	38.5	37.1	38.6	38.5	35.2
9	53.5	53.4	53.2	53.5	53.0	52.8	54.2
10	36.2	36.2	36.2	36.2	36.1	36.2	36.4
11	21.6	21.6	21.6	21.6	21.6	21.6	21.5
12	39.4	38.9	39.5	38.8	39.4	38.8	38.4
13	83.1	85.4	84.4	86.3	85.1	84.7	83.3
14	46.4	46.7	46.3	46.3	46.3	45.8	48.6
15	19.8	26.8	29.1	28.2	30.5	38.1	145.4
16	28.7	68.6	65.6	68.3	64.5	190.3	121.6
17	170.9	168.5	168.3	174.8	174.8	157.4	163.7
18	20.1	20.7	19.5	21.1	19.3	20.6	18.5
19	12.0	12.0	12.0	12.1	12.0	12.0	12.0



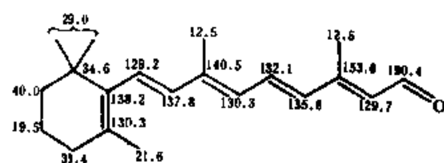
38. R = H
39. R = β-OAc
40. R = α-OAc
41. R = β-OH
42. R = α-OH



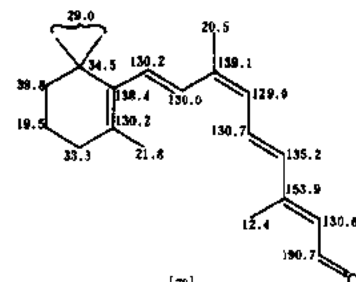
43



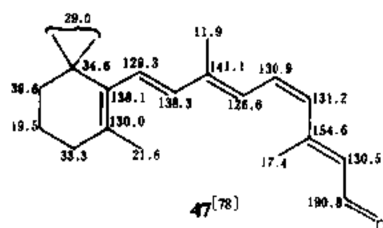
44



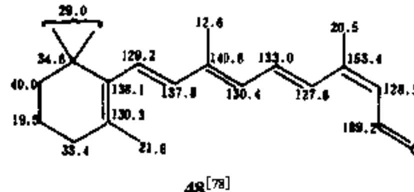
45[77]



46[78]

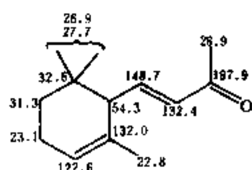


47[78]

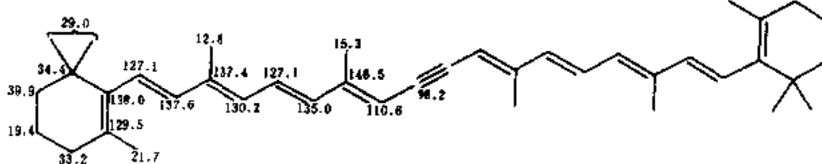


48[78]

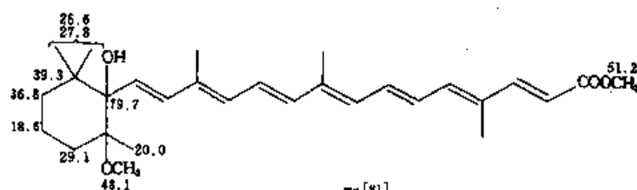
六、四萜类化合物^{13}C-NMR化学位移



49[79]



50[80]



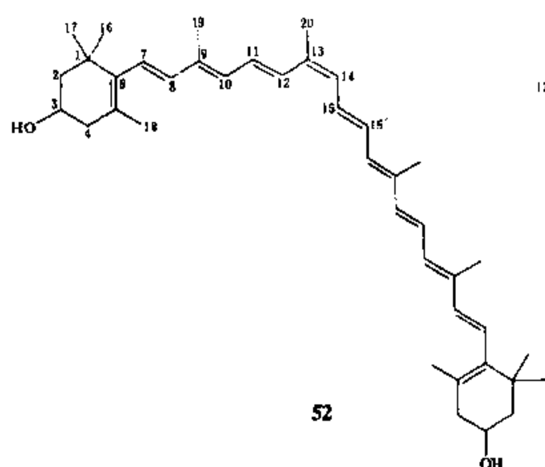
51[81]

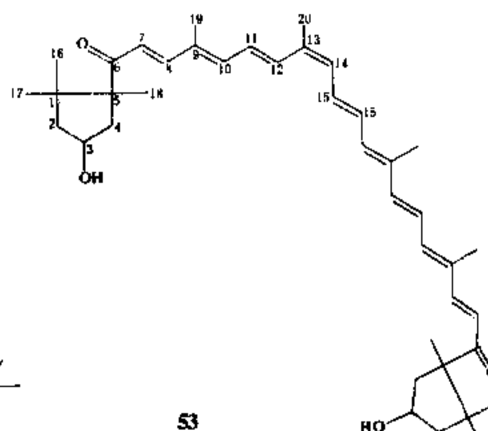
表 21-56　玉米黄素和辣椒红素及衍生物 52～57 的^{13}C-NMR 化学位移数据[82]

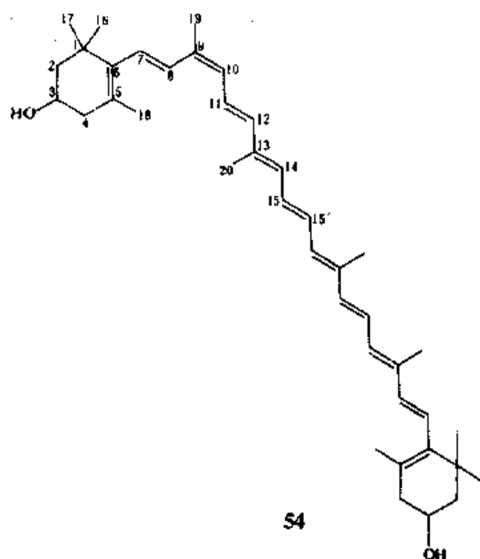
化合物 / C	52		53		54		55		56	57
	反式末端	顺式末端	反式末端	顺式末端	反式末端	顺式末端	反式末端	顺式末端		
1	37.18	37.18	44.0	44.0	37.16	37.16	44.03	44.03	36.73	44.42
2	48.66	48.66	50.93	50.93	48.64	48.64	50.95	50.95	44.24	51.03
3	65.15	65.15	70.37	70.37	65.16	65.16	70.40	70.40	68.47	70.35
4	42.72	42.72	45.36	45.36	42.71	42.71	45.41	45.41	38.57	45.46
5	126.37	126.26	59.01	59.01	126.22	126.47	59.00	59.01	125.66	59.01
6	137.92	137.92	203.0	203.0	137.90	138.15	202.98	203.55	138.03	203.0
7	125.71	125.71	121.19	121.55	125.68	127.52	121.17	122.58	125.36	121.27
8	138.58	138.58	146.85	146.75	138.56	130.86	146.87	138.10	138.73	146.87

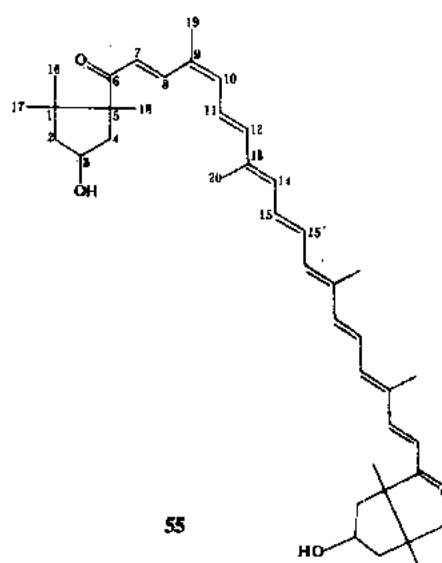
续表

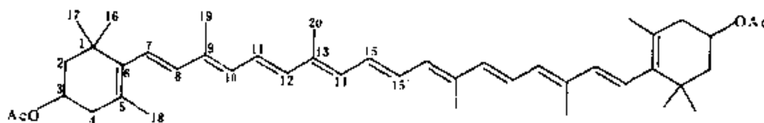
化合物 / C	52		53		54		55		56	57
	反式末端	顺式末端	反式末端	顺式末端	反式末端	顺式末端	反式末端	顺式末端		
9	135.63	135.71	133.97	134.07	135.67	134.28	133.98	132.15	135.55	134.10
10	131.38	131.38	140.38	140.58	131.38	129.91	140.59	139.09	131.52	140.50
11	124.96	126.05	124.52	125.88	124.98	123.79	124.54	123.70	124.96	124.67
12	137.70	129.43	141.84	133.38	137.65	136.38	141.87	140.59	137.74	141.75
13	136.43	134.92	136.73	135.24	136.38	136.90	136.70	137.26	136.46	137.00
14	132.57	131.02	134.82	133.28	132.63	132.49	135.07	134.35	132.68	134.99
15	130.19	128.93	131.05	129.90	130.05	130.14	130.86	131.42	130.18	103.25
16	28.82	28.82	25.12	25.12	28.89	28.89	25.13	25.13	28.58	25.14
17	30.34	30.34	25.93	25.93	30.34	30.34	25.90	25.90	30.07	25.94
18	21.59	21.59	21.34	21.34	21.59	21.69	21.35	21.27	21.40	21.37
19	12.78	12.78	12.87	12.87	12.83	20.70	12.89	20.44	12.75	12.83
20	12.78	20.68	12.87	20.61	12.83	12.83	12.84	13.00	12.75	12.83
$OCOCH_3$									21.39	
OCO									170.63	


52

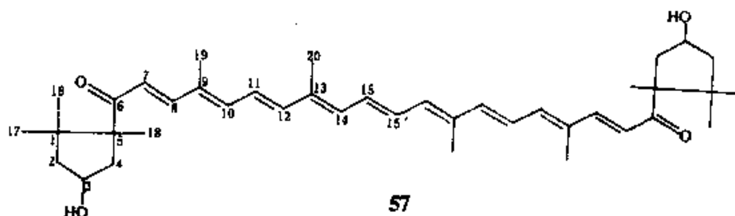

53


54


55



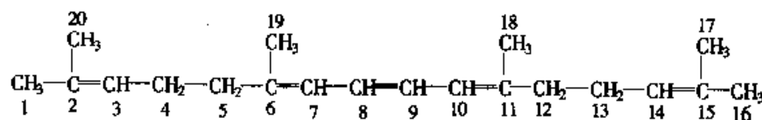
56



57

表 21-57　二十碳五烯化合物 58～63 的 ^{13}C-NMR 化学位移数据[83]

C \ 化合物	58	59	60	61	62	63
1	25.67	25.85	25.73	25.73	25.67	25.79
2	131.52	132.57	131.80	131.87	131.75	132.28
3	124.03	123.15	124.10	123.97	124.03	123.39
4	26.67	26.84	26.96	26.90	26.90	27.02
5	40.12	40.58	32.19	32.34	32.63	32.34
6	137.95	139.65	138.30	139.53	137.89	139.53
7	125.44	120.00	126.25	120.87	126.20	120.82
8	127.18	123.27	126.84	122.80	127.01	122.86
9	127.18	123.27	126.84	122.80	127.01	122.86
10	125.44	120.00	126.25	120.87	125.43	120.02
11	137.95	139.65	138.30	139.53	137.66	139.76
12	40.12	40.58	32.69	32.34	40.12	40.53
13	26.67	26.84	26.96	26.90	26.67	27.02
14	124.03	123.15	124.10	123.97	124.03	123.15
15	131.52	132.57	131.80	131.87	131.52	131.51
16	25.67	25.85	25.73	25.73	25.67	25.79
17	17.66	17.89	17.72	17.66	17.66	17.84
18	16.72	16.55	23.98	24.33	16.72	16.49
19	16.72	16.55	23.98	24.33	23.98	24.33
20	17.66	17.89	17.72	17.66	17.66	17.84



58. 全反式　　**60.** 6-*cis*，8-*trans*，10-*cis*　　**62.** 6-*cis*，8-*trans*，10-*cis*

59. 6-*trans*，8-*cis*，10-*trans*　　**61.** 全顺式　　**63.** 6-*cis*，8-*cis*，10-*trans*

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第二十二章　色原酮类衍生物的^{13}C-NMR化学位移

色原酮类衍生物的^{13}C-NMR谱中化学位移具有如下特征。

① 主要化学位移区域　黄酮类化合物各碳的化学位移主要出现在δ=40～200之间，大约可分为如下几个区域：δ=40～85区域为二氢黄酮、二氢异黄酮和二氢黄酮醇的C-2和C-3以及甲氧基；δ=90～100区域为黄酮、异黄酮、二氢黄酮、二氢黄酮醇、异黄烷的C-6、C-8和三取代B环的两个无取代的碳以及黄酮的C-3；δ=110～140区域为单取代或二取代B环的碳；δ=135～168区域为苯环的连氧碳；δ=168～200区域为羰基碳的化学位移。

② 5位羟基取代的影响　5位无羟基取代的黄酮和异黄酮的羰基碳化学位移大约在175～177.5,黄酮醇的羰基碳化学位移大约在172.5，二氢黄酮、二氢异黄酮和二氢黄酮醇的羰基碳化学位移大约在190～192.5；5位有羟基取代的黄酮和异黄酮的羰基碳化学位移大约在181±1，黄酮醇的羰基碳化学位移大约在175～176，二氢黄酮和二氢异黄酮以及二氢黄酮醇的羰基碳化学位移大约在197±1。

③ C环C-2和C-3的特点　黄酮的C-2化学位移在160～165.5，C-3化学位移在104～112；异黄酮的C-2化学位移在149.8～156.5，C-3化学位移在123～126；黄酮醇的C-2化学位移在146～149.5，C-3化学位移在135～138；二氢黄酮的C-2化学位移在75～80.5，C-3化学位移在42.5～45；二氢异黄酮的C-2化学位移在70～72，C-3化学位移在44～45；二氢黄酮醇的C-2化学位移在83～84.5，C-3化学位移在71～73.5。

④ 黄烷类化合物的化学位移　黄烷类化合物的^{13}C-NMR谱中C-2、C-3和C-气的化学位移分别为78.7、25.1和31.3；而异黄烷类化合物中C-3向低场位移约7个δ单位，C-2向高场位移约8个δ单位，而C-4几乎不变。

⑤ 查耳酮和二氢查耳酮的化学位移　查耳酮和二氢查耳酮的^{13}C-NMR谱中羰基碳的化学位移前者在188～194.6，后者向高场位移约5.5个δ单位，对于C-α和C-β前者化学位移分别为116.6～128.1个化学位移单位和136.2～145.4个化学位移单位，而后者化学位移分别为大约44.5和30。

第一节　黄酮及黄酮醇类化合物的^{13}C-NMR化学位移

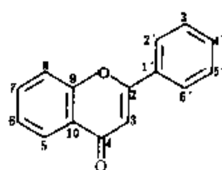
一、黄酮类化合物的^{13}C-NMR化学位移

表22-1　黄酮类化合物1～12的^{13}C-NMR化学位移数据[1,2,3,4]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
2	163.2	164.0	160.6		162.66	162.6	162.6	160.8	160.6	162.8	163.1	163.0
3	107.6	105.6	108.7	106.7	106.5	107.2	107.1	111.1	112.5	107.5	104.9	105.9
4	178.4	182.9	177.8		176.1	177.4	178.0	177.3	178.7	178.0	176.9	177.9
5	125.7	155.8	159.4	104.8	126.3	126.7	114.2	125.2	125.4	125.4	125.3	125.3
6	125.2	107.2	109.8		114.9	114.1	124.6	124.8	124.6	124.9	124.8	124.7
7	133.7	135.6	133.4	123.6	161.7	163.7	116.1	134.1	133.3	133.2	133.9	133.0
8	118.1	110.8	106.2	119.4	102.4	100.2	148.8	118.5	117.8	117.9	118.3	117.7

续表

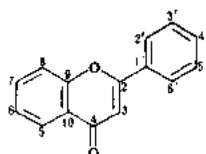
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
9	156.3	159.8	157.9		157.3	157.7	146.0	155.9	156.2	155.9	155.6	155.8
10	124.0	110.3	114.0		116.0	117.6	124.0	123.2		123.7	123.4	123.7
1′	131.8	130.5	131.9		131.1	131.6	131.6	117.8	132.8		121.7	131.9
2′	126.3	126.3	125.6	126.1	126.0	125.8	126.1	156.7	157.8	111.5	128.4	127.7
3′	129.0	128.9	128.6	128.9	128.9	128.7	128.7	117.1	111.6	159.7	116.0	114.2
4′	131.6	131.9	131.0	131.3	131.3	131.1	131.2	132.6	132.2	116.9	161.0	162.1
5′	129.0	128.9	128.6	128.9	128.9	128.7	128.7	119.5	120.5	129.8	116.0	114.2
6′	126.3	126.3	125.6	126.1	126.0	125.8	126.1	128.6	129.1	118.5	128.4	127.7



1. —
2. 5-OH
3. 5-OCH_3
4. 6-OCH_3
5. 7-OH
6. 7-OCH_3
7. 8-OCH_3
8. 2′-OH
9. 2′-OCH_3
10. 3′-OCH_3
11. 4′-OH
12. 4′-OCH_3

表 22-2 黄酮类化合物 13～24 的^{13}C-NMR 化学位移数据[1,3,4,5]

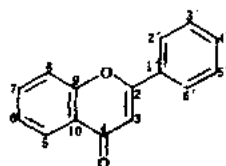
C \ 化合物	13	14	15	16	17	18	19	20	21	22	23	24
2	163.4	163.5	165.4	164.1	162.7	161.9	162.4	160.0	165.4	163.9	160.4	164.6
3	103.6	105.4	103.9	104.0	104.7	105.2	105.3	106.1	104.3	103.9	107.1	103.4
4	181.1	182.1	183.4	182.5	176.6	176.4	176.4	178.1	183.1	182.3	175.7	182.3
5	161.7	161.3	156.4	155.7	126.6	126.5	126.2	141.2	158.6	157.9	159.0	157.7
6	99.1	98.2	108.0	106.9	115.0	114.6	114.6	116.5	95.5	99.4	96.4	98.2
7	164.4	165.4	136.1	135.1	162.7	162.7	163.9	160.9	164.9	164.8	162.4	165.6
8	94.2	92.8	111.4	110.5	102.7	102.6	101.0	100.7	100.9	94.3	95.2	92.9
9	157.5	157.4	160.1	159.7	157.6	157.5	157.5	158.5	109.0	162.2	159.9	161.8
10	104.0	105.0	110.4	109.9	116.3	116.2	117.2	114.2	105.0	104.4	106.0	105.0
1′	122.9	130.6	121.9	119.2	122.0	123.5	123.4	123.0	122.7	123.5	121.5	121.6
2′	128.2	126.5	129.1	128.1	128.3	127.9	128.1	127.5	129.7	128.4	127.7	128.8
3′	114.6	129.2	116.7	114.5	116.1	114.5	114.6	114.2	117.3	114.8	115.8	116.3
4′	162.4	132.1	161.6	163.3	160.9	162.1	162.1	161.5	161.7	162.8	160.6	161.8
5′	114.6	129.2	116.7	114.5	116.1	114.5	114.6	114.2	117.3	114.8	115.8	116.3
6′	128.2	126.5	129.1	128.1	128.3	127.9	128.1	125.5	129.7	128.4	127.7	128.8



13. 5-OH, 7-OH
14. 5-OH, 7-OCH_3
15. 5-OH, 4′-OH
16. 5-OH, 4′-OCH_3
17. 7-OH, 4′-OH
18. 7-OH, 4′-OCH_3
19. 7-OCH_3, 4′-OCH_3
20. 5-CH_3, 7-OH, 4′-OCH_3
21. 5-OH, 7-OH, 4′-OH
22. 5-OH, 4′-OH, 7-OCH_3
23. 5-OH, 7-OH, 4′-OCH_3
24. 5-OCH_3, 7-OH, 4′-OH

表 22-3　黄酮类化合物 25 ~ 34 的 ^{13}C-NMR 化学位移数据[1,4,5,6]

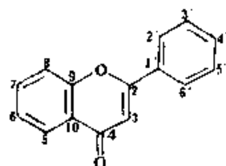
C \ 化合物	25	26	27	28	29	30	31	32	33	34
2	164.1	162.6	164.7	164.5	163.7	163.6	158.8	157.7	163.7	162.4
3	105.3	105.7	104.2	103.3	103.8	104.0	105.4	108.3	105.1	106.9
4	177.9	176.6	182.6	182.2	181.8	181.8	182.6	177.0	177.0	177.1
5	125.1	125.0	155.7	157.9	157.4	157.5	152.9	152.5	125.4	125.5
6	125.0	124.6	109.9	99.2	98.8	99.0	132.6	140.4	125.0	124.8
7	134.4	133.6	135.1	164.7	164.2	164.4	163.9	162.0	134.2	134.2
8	118.4	118.1	110.5	94.2	94.0	94.0	90.3	96.3	118.2	118.7
9	156.1	155.6	159.7	162.1	161.6	161.7	153.2	154.5	155.7	155.7
10	123.5	123.7	109.9	104.2	103.3	103.7	106.2	112.2	123.5	123.3
1′	122.8	123.3	122.9	119.3	120.4	118.7	131.1	131.5	121.1	126.5
2′	113.1	110.5	110.5	113.8	110.2	113.1	126.1	125.9	105.9	104.2
3′	145.8	149.3	149.2	146.2	150.8	146.9	129.0	128.9	146.6	153.3
4′	149.5	152.2	152.6	150.1	148.0	151.2	131.8	131.2	137.8	140.8
5′	116.2	112.4	119.3	116.4	115.8	112.1	129.0	128.9	146.6	153.3
6′	119.4	119.9	120.2	122.1	121.7	123.3	126.1	125.9	105.9	104.2



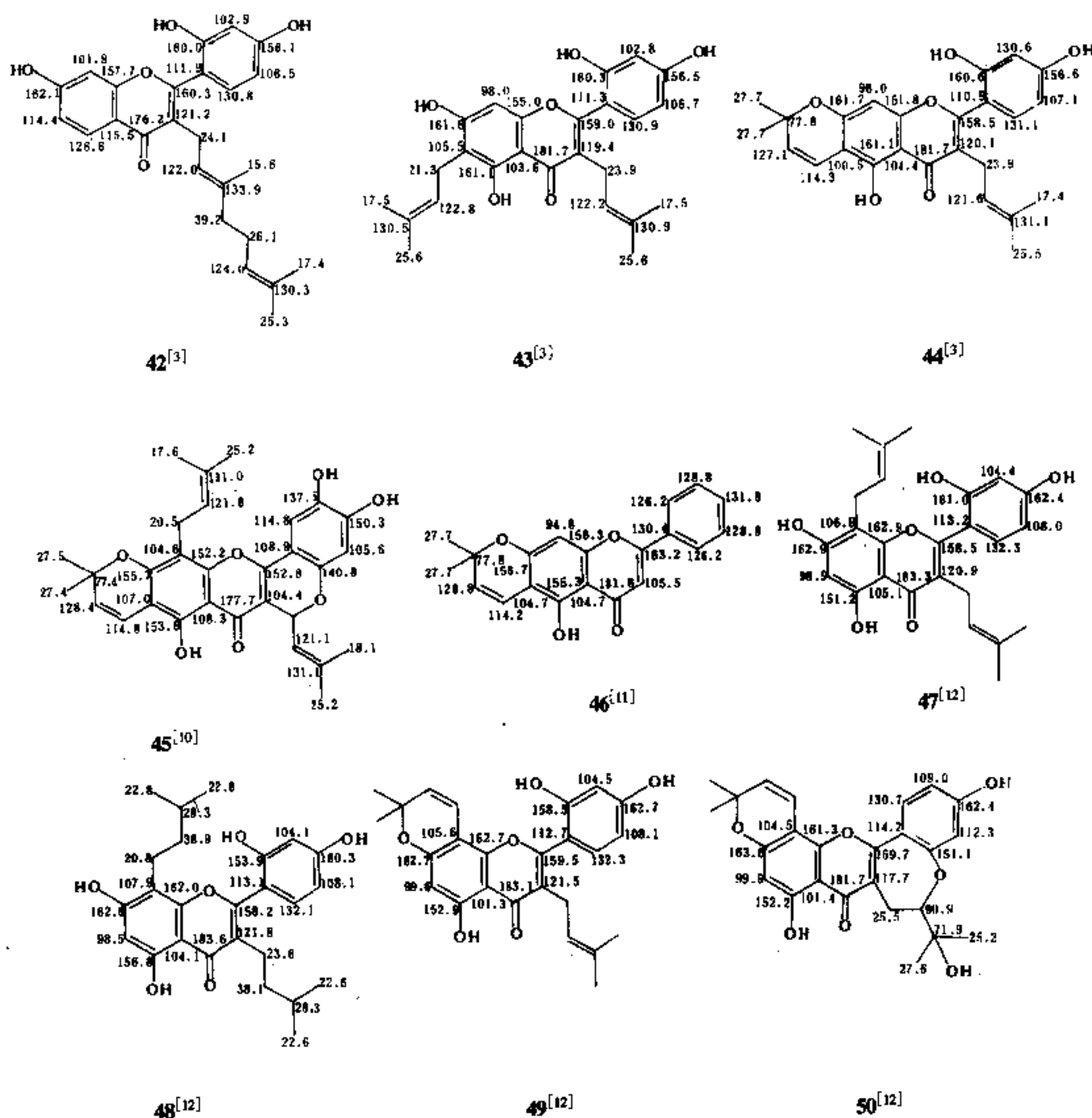
25. 3′-OH，4′-OH
26. 3′-OCH_3，4′-OCH_3
27. 5-OH，3′-OCH_3，4′-OCH_3
28. 5-OH，7-OH，3′-OH，4′-OH
29. 5-OH，7-OH，4′-OH，3′-OCH_3
30. 5-OH，7-OH，3′-OH，4′-OCH_3
31. 5-OH，6-OCH_3，7-OCH_3
32. 5-OCH_3，6-OCH_3，7-OCH_3
33. 3′-OH，4′-OH，5′-OH
34. 3′-OCH_3，4′-OCH_3，5′-OCH_3

表 22-4　黄酮类化合物 35 ~ 41 的 ^{13}C-NMR 化学位移数据[4,7,8,9]

C \ 化合物	35	36	37	38	39	40	41
2	163.1	161.8	164.2	164.0	164.2	160.6	163.6
3	104.8	106.6	103.2	103.6	103.9	100.3	102.6
4	176.6	176.5	181.6	181.6	181.7	177.1	182.0
5	126.8	126.7	161.6	157.2	161.4	151.5	152.5
6	115.1	115.0	99.0	98.7	99.0	138.3	131.1
7	162.8	162.7	164.2	163.5	163.0	147.6	152.3
8	102.5	103.8	93.9	94.1	94.2	138.0	94.1
9	157.6	157.5	157.5	161.3	157.4	148.3	157.3
10	116.3	116.2	104.0	120.8	104.8	114.8	103.9
1′	121.4	126.5	120.9	139.7	125.9	125.9	120.4
2′	105.7	104.0	106.0	104.3	104.8	107.2	104.2
3′	146.5	153.3	146.5	148.0	153.2	144.1	148.1
4′	137.5	140.5	137.9	164.0	141.4	149.6	139.7
5′	146.5	153.3	146.5	148.0	153.2	143.8	148.1
6′	105.7	104.0	106.0	104.3	104.8	106.7	104.2



35. 5-OH，3′-OH，4′-OH，5′-OH
36. 5-OH，3′-OCH_3，4′-OCH_3，5′-OCH_3
37. 5-OH，7-OH，3′-OH，4′-OH，5-OH
38. 5-OH，7-OH，3′-OCH_3，4′-OH，5′-OCH_3
39. 5-OH，7-OH，3′-OCH_3，4′-OCH_3，5′-OCH_3
40. 5-OCH_3，6-OCH_3，7-OCH_3，8-OCH_3，5′-OCH_3，3′，4′-（OCH_2O）
41. 5-OH，7-OH，4′-OH，6-OCH_3，3′-OCH_3，5′-OCH_3



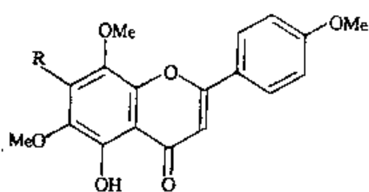
42[3]　43[3]　44[3]

45[10]　46[11]　47[12]

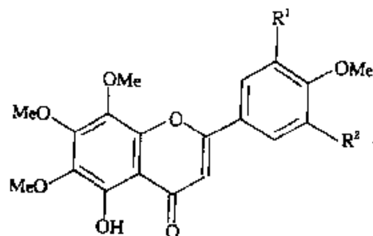
48[12]　49[12]　50[12]

表 22-5　黄酮化合物 51～57 的^{13}C-NMR 化学位移数据[61]

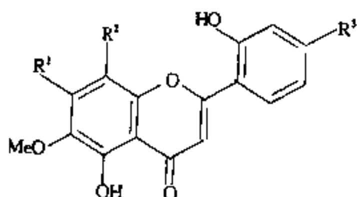
C ╲ 化合物	51	52	53	54	55	56	57
2	162.8	152.9	163.7	163.5	166.2	165.7	163.2
3	103.8	104.6	103.9	102.4	105.1	104.4	102.9
4	183.0	182.7	183.5	184.5	185.3	184.0	182.1
5	149.6	145.6	149.7	152.5	159.5	158.7	150.8
6	133.1	132.8	140.3	133.6	133.7	125.1	131.5
7	164.1	163.5	164.5	163.5	166.2	158.3	163.3
8	136.6	136.4	148.2	141.2	140.9	113.9	145.3
4a	107.0	106.8	103.9	102.4	105.1	105.3	112.7
8a	145.8	149.3	149.7	152.5	159.5	151.3	151.1
1′	123.5	126.1	124.3	127.4	127.6	129.0	127.9
2′	128.1	103.6	128.9	106.6	107.1	148.3	146.8
3′	114.7	153.4	115.4	149.6	152.6	100.3	102.9
4′	153.0	141.5	152.1	149.4	150.7	152.7	148.2
5′	114.7	153.4	115.4	149.6	152.6	112.8	118.5
6′	128.1	103.6	128.9	104.9	107.1	120.1	123.0
OMe	55.6	56.1	55.9	56.0	60.9	56.0	55.7
	61.1	60.8	60.6	61.1	61.5	62.1	60.0
	61.7	60.9	61.7	61.3	62.3		61.2
	62.1	61.5		61.6	62.7		
		61.8		62.0			



51. R = OMe
53. R = OH



52. $R^1 = R^2 = OMe$
54. $R^1 = OH$, $R^2 = OMe$
55. $R^1 = R^2 = OH$

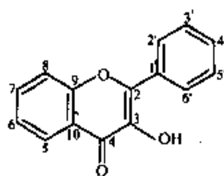


56. $R^1 = OH$, $R^2 = H$, $R^3 = OMe$
57. $R^1 = R^2 = OMe$, $R^3 = OH$

二、黄酮醇类化合物的^{13}C-NMR化学位移

表 22-6　黄酮醇类化合物 1～9 的^{13}C-NMR 化学位移数据[1,13,14,15]

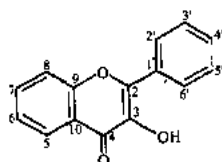
C \ 化合物	1	2	3	4	5	6	7	8	9
2	147.8	145.3	146.1	146.1	149.6	146.9	142.0	147.3	146.7
3	138.1	137.8	137.9	135.5	136.4	135.8	137.1	136.0	136.4
4	173.8	172.8	176.5	175.7	176.7	175.9	171.1	175.9	176.0
5	125.4	124.0	162.3	156.0	156.9	156.2	158.1	156.0	156.0
6	125.4	124.4	99.1	98.2	94.9	98.3	96.0	97.4	97.4
7	134.5	133.0	165.3	163.8	164.1	164.0	162.6	164.9	164.9
8	118.8	117.9	94.6	93.4	99.5	93.5	94.8	91.8	91.8
9	155.4	154.3	157.7	160.5	161.3	160.8	160.6	160.4	160.4
10	121.5	121.1		102.9	104.9	103.1	105.2	103.7	104.0
1′	123.4	123.3	132.3	121.6	111.1	122.1	122.4	121.9	123.4
2′	116.3	112.3	129.4	129.3	158.0	115.2	144.6	115.2	114.8
3′	145.4	148.7	128.5	115.3	104.9	145.1	145.1	145.0	146.2
4′	148.0	150.7	130.8	159.0	160.4	147.7	147.1	147.8	149.4
5′	116.7	112.2	128.5	115.3	109.2	115.7	115.7	115.6	111.7
6′	121.7	121.5	129.4	129.3	132.3	120.1	119.3	120.1	119.8



1. 3′-OH, 4′-OH
2. 3′-OCH_3, 4′-OCH_3
3. 5-OH, 7-OH
4. 5-OH, 7-OH, 4′-OH
5. 5-OH, 7-OH, 4′-OH, 2′-OH
6. 5-OH, 7-OH, 3′-OH, 4′-OH
7. 5-OCH_3, 7-OH, 3′-OH, 4′-OH
8. 5-OH, 7-OCH_3, 3′-OH, 4′-OH
9. 5-OH, 7-OCH_3, 3′-OH, 4′-OCH_3

表 22-7　黄酮醇类化合物 10～18 的^{13}C-NMR 化学位移数据[3,16,17,18]

C \ 化合物	10	11	12	13	14	15	16	17	18
2	150.1	153.3	152.0	151.4	151.8	155.2	155.3	154.9	147.1
3	137.4	137.9	141.4	138.0	133.8	138.9	138.1	138.6	136.1
4	171.6	172.6	173.6	180.0	172.7	178.2	178.1	178.1	176.0
5	158.6	126.4	160.5	151.9		161.4	161.5	161.3	161.0
6	95.5	114.7	95.5	131.5	140.0	94.8	98.8	98.7	98.5
7	164.1	164.4	163.5	158.0	140.4	164.5	164.4	164.4	164.2
8	92.2	100.0	92.1	89.8	92.8	93.9	94.0	94.1	93.5
9	160.4	157.2	158.4	155.0	152.6	156.7	156.5	156.5	156.4
10	106.0	114.7	109.1	105.7	119.6	104.6	104.5	104.4	103.3
1′	123.6	126.7	130.5	122.1	129.8	130.2	154.5	125.2	121.2
2′	110.2	105.6	127.7	110.7	127.4	128.2	130.1	106.0	107.5
3′	148.6	153.3	128.0	148.0	127.8	128.8	114.3	152.8	146.0
4′	148.6	140.1	129.0	150.8	129.6	131.1	161.5	140.0	136.1
5′	110.8	153.3	128.1	110.3	127.8	128.8	114.3	152.8	146.0
6′	120.5	105.6	128.7	121.5	127.8	128.2	130.1	106.0	136.1



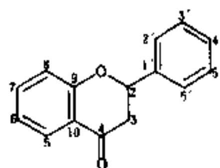
10. 5-OCH_3，7-OCH_3，3′-OCH_3，4′-OCH_3
11. 7-OCH_3，3′-OCH_3，4′-OCH_3，5′-OCH_3
12. 3-OCH_3，5-OCH_3，7-OCH_3
13. 3-OCH_3，6-OCH_3，7-OCH_3，3′-OCH_3，4′-OCH_3，5-OH
14. 3-OCH_3，5-OCH_3，6，7-（OCH_2O）
15. 3-OCH_3，5-OH，7-OH
16. 3-OCH_3，4′-OCH_3，5-OH，7-OH
17. 3-OCH_3，5-OH，7-OH，3′-OCH_3，4′-OCH_3，5′-OCH_3
18. 5-OH，7-OH，3′-OH，4′-OH，5′-OH

第二节　二氢黄酮及二氢黄酮醇类化合物^{13}C-NMR 化学位移

一、二氢黄酮类化合物的^{13}C-NMR 化学位移

表 22-8　二氢黄酮类化合物 1～9 的^{13}C-NMR 化学位移数据[6,19]

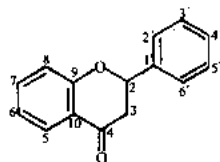
C \ 化合物	1	2	3	4	5	6	7	8	9
2	72.4	79.7	75.1	74.9	79.6	79.3	79.5	80.3	79.0
3	44.6	44.1	43.4	42.6	44.1	43.7	43.9	44.2	45.6
4	191.6	190.0	191.4	190.3	189.9	189.7	190.2	190.4	189.2
5	126.9	128.5	128.8	128.1	128.4	128.1	128.4	128.5	156.2
6	121.4	110.0	110.1	109.7	109.9	109.7	109.8	110.2	89.5
7	135.9	165.8	166.1	165.6	165.8	165.7	165.8	166.4	158.7
8	117.9	100.7	101.0	100.8	100.8	100.9	100.7	101.4	131.0
9	161.3	163.2	164.1	163.6	163.1	163.1	163.2	164.0	157.8
10	120.8	114.6	115.0	114.5	114.6	114.6	114.6	115.2	106.3
1′	138.6	138.6	127.6	125.3	140.2	140.2	130.6	130.0	138.9
2′	125.9	125.9	155.9	154.2	111.7	113.2	127.5	128.5	125.9
3′	128.6	128.5	110.6	115.5	159.7	157.6	113.9	115.8	128.7
4′	128.6	128.5	129.4	129.0	113.7	115.5	159.6	158.6	128.4
5′	128.6	128.5	120.9	119.0	129.6	129.5	113.9	115.8	128.7
6′	125.9	128.9	126.4	126.5	118.1	116.8	127.5	128.5	125.9



1.
2. 7-OCH_3
3. 7-OCH_3，2'-OCH_3
4. 7-OCH_3，2'-OH
5. 7-OCH_3，3'-OH
6. 7-OCH_3，3'-OH
7. 7-OH，4'-OH
8. 7-OCH_3，4'-OH
9. 5-OCH_3，7-OCH_3，8-OCH_3

表 22-9　二氢黄酮类化合物 10～18 的 ^{13}C-NMR 化学位移数据[15,20,21]

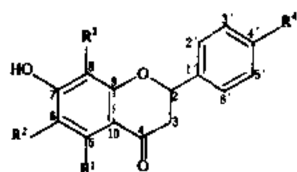
C \ 化合物	10	11	12	13	14	15	16	17	18
2	78.4	78.4	77.8	79.0	79.0	78.3	78.7	78.5	77.5
3	42.2	42.0	41.9	43.2	45.5	42.2	42.1	42.1	44.8
4	195.8	196.2	196.1	196.0	189.21	196.2	196.3	196.2	192.0
5	163.6	163.6	163.5	164.2	165.1	163.4	163.5	163.8	140.4
6	96.1	95.9	95.8	95.1	93.7	95.7	95.7	96.2	125.3
7	166.6	166.7	166.6	168.0	166.0	166.6	166.6	166.9	145.1
8	95.1	95.0	94.9	94.2	93.2	94.8	95.0	95.4	115.6
9	162.7	162.9	162.7	162.9	162.4	162.8	162.9	163.0	162.6
10	101.9	101.8	101.7	103.2	106.1	101.7	101.8	102.1	126.2
1'	138.0	138.0	128.9	130.6	131.0	130.5	129.4	131.4	131.0
2'	126.5	128.2	128.6	127.7	127.7	114.2	111.1	114.3	127.4
3'	128.5	115.2	113.5	114.3	114.2	145.1	147.5	146.7	113.1
4'	128.5	157.8	159.4	160.1	160.0	145.6	146.9	148.1	159.3
5'	128.5	115.2	113.5	114.3	114.2	115.3	115.2	112.1	113.1
6'	126.5	128.2	128.6	127.7	127.7	117.8	119.6	118.0	127.4



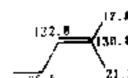
10. 5-OH，7-OH
11. 5-OH，7-OH，4'-OH
12. 5-OH，7-OH，4'-OCH_3
13. 5-OH，7-OCH_3，4'-OCH_3
14. 5-OCH_3，7-OCH_3，4'-OCH_3
15. 5-OH，7-OH，3'-OH，4'-OH
16. 5-OH，7-OH，4'-OH，3'-OCH_3
17. 5-OH，7-OH，3'-OH，4'-OCH_3
18. 5-CH_3，7-CH_3，4'-OCH_3

表 22-10　二氢黄酮类化合物 19～27 的 ^{13}C-NMR 化学位移数据[22,23]

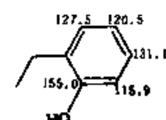
C \ 化合物	19	20	21	22	23	24	25	26	27
2	78.3	78.8	79.7	79.9	77.6	79.9	77.8	80.0	79.7
3	42.0	43.0	43.6	43.4	44.7	43.5	44.7	43.4	43.6
4	197.1	191.0	196.7	197.2	187.6	197.5	188.3	197.0	197.2
5	161.1	125.4	162.1	163.3	162.2	160.6	160.0	162.0	163.3
6	107.1	113.8	108.2	96.8	93.2	108.6	114.6	110.1	96.5
7	164.7	162.1	164.9	164.8	160.1	162.4	160.3	165.0	165.1
8	95.4	109.8	95.9	107.2	106.4	107.6	110.5	95.4	108.9
9	160.1	160.8	162.1	161.1	161.7	159.5	158.3	160.8	161.2
10		115.1	103.0	103.4	104.9	103.4	108.4	103.1	103.1
1'	129.5	129.8	139.9	140.0	139.4	139.9	139.3	140.3	130.7
2'	128.3	128.2	127.0	127.1		127.0		130.3	128.9
3'	115.4	115.3	129.3	129.4		129.3		129.4	116.1
4'	157.9	157.7	129.1	129.1		129.1		130.3	158.7
5'	115.4	115.3	129.3	129.4		129.3		129.4	116.1
6'	128.3	128.2	127.0	127.1		127.1		130.3	128.1



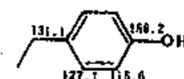
19. $R^1 = R^4 = OH$, $R^3 = H$, $R^2 =$
20. $R^1 = R^2 = H$, $R^4 = OH$, $R^3 =$

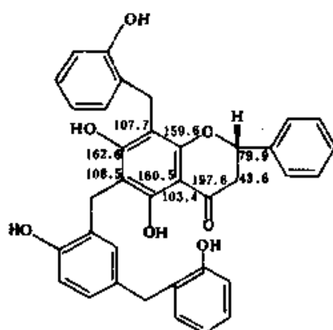


21. $R^1 = OH$, $R^3 = R^4 = H$, $R^2 =$
22. $R^1 = OH$, $R^2 = R^4 = H$, $R^3 =$
23. $R^1 = OCH_3$, $R^2 = R^4 = H$, $R^3 =$
24. $R^1 = OH$, $R^4 = H$, $R^2 = R^3 =$
25. $R^1 = OCH_3$, $R^4 = H$, $R^2 = R^3 =$

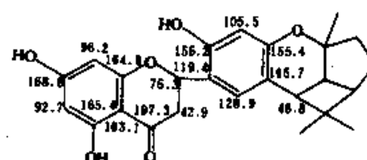


26. $R^1 = OH$, $R^3 = R^4 = H$, $R^2 =$
27. $R^1 = OH$, $R^2 = R^4 = H$, $R^3 =$

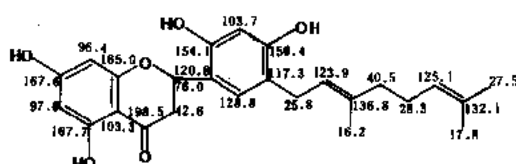




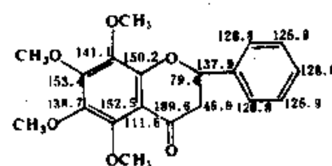
28[24]



29[25]



30[26]

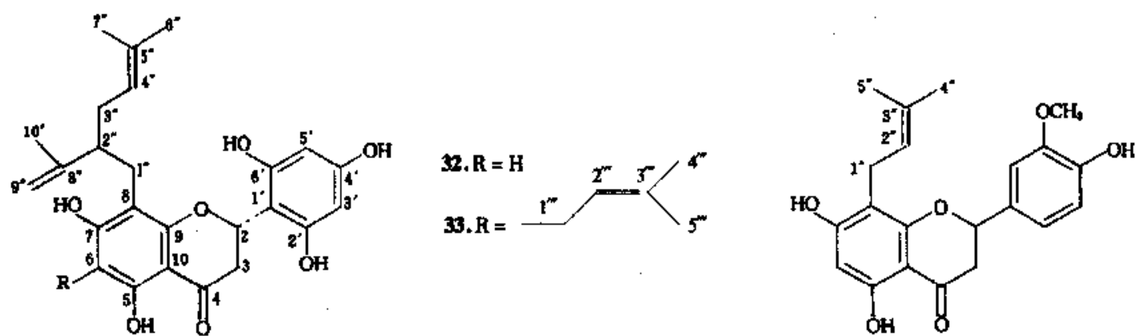


31[27]

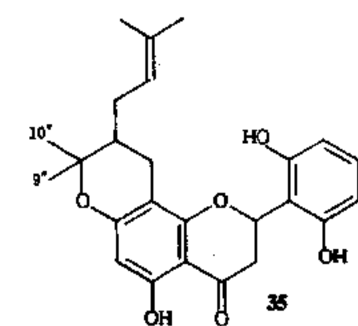
表 22-11　二氢黄酮化合物 32 ~ 36 的^{13}C-NMR 化学位移数据[62]

C ╲ 化合物	32	33	34	35	36
2	73.7	73.9	80.1	74.1	73.9
3	41.2	41.4	43.8	40.6	40.7
4	199.1	199.5	197.7	198.0	198.7
5	163.1	160.1	163.1	163.0	163.4
6	96.1	108.1	96.5	97.2	97.1
7	165.0	162.4	165.1	163.2	165.8
8	108.0	107.8	108.4	103.8	108.0
9	162.6	161.1	161.2	161.9	162.0
10	103.2	103.3	103.4	102.8	103.3
1′	104.1	104.2	129.8	111.8	112.2
2′	158.6	158.8	111.1	157.7	157.7
3′	96.4	96.2	148.6	108.9	108.7
4′	159.9	160.1	147.9	131.0	130.9
5′	96.4	96.2	115.8	108.9	108.7
6′	158.6	158.8	120.4	157.7	157.7
1″	27.5	27.8	22.4	22.5	28.3

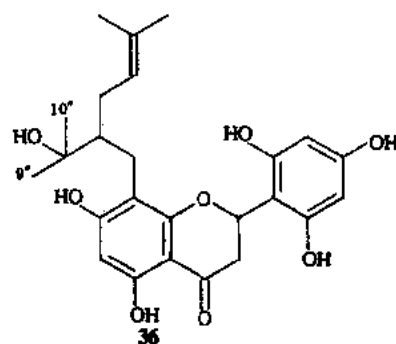
C ╲ 化合物	32	33	34	35	36
2″	47.8	47.7	123.8	41.7	51.2
3″	32.4	31.9	131.4	30.4	32.5
4″	124.5	124.5	26.0	123.3	125.9
5″	131.6	131.8	18.0	133.8	130.9
6″	25.8	26.0		26.2	26.0
7″	18.4	17.9		18.6	17.9
8″	149.23	149.2		80.0	74.5
9″	111.1	111.5		27.8	29.1
10″	19.1	19.3		21.3	29.1
1‴		22.6			
2‴		123.4			
3‴		132.3			
4‴		26.1			
5‴		18.1			
OCH_3			56.4		



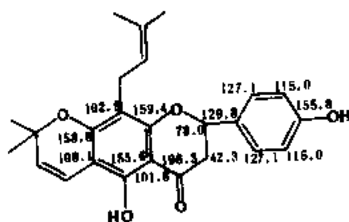
34



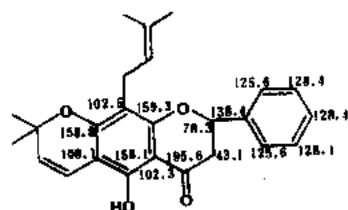
35



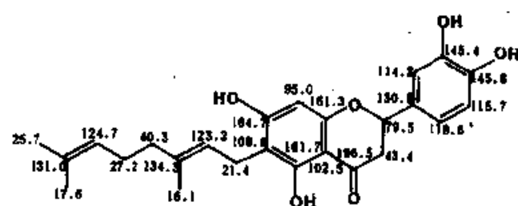
36



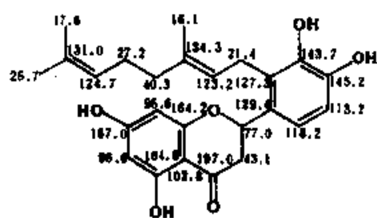
37[28]



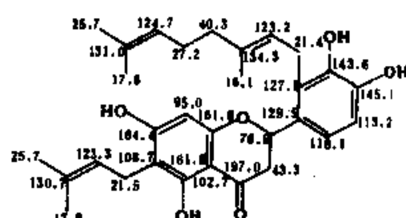
38[28]



39[29]



40[29]

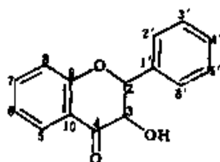


41[29]

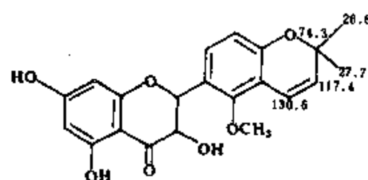
二、二氢黄酮醇类化合物的¹³C-NMR化学位移

表 22-12　二氢黄酮醇类化合物 1～11 的¹³C-NMR 化学位移数据[3,16,21,22,28,30,31]

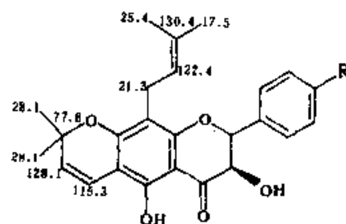
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
2	83.1	83.6	84.3	75.5	78.3	82.7	84.3	83.4	84.5	85.6	80.6
3	71.7	72.5	73.0	73.4	70.9	71.5	73.1	72.9	73.1	72.0	72.9
4	197.1	189.7	192.2	195.0	198.4	197.3	197.7	190.8	197.9	195.7	184.9
5	163.3	163.7	128.9	165.0	163.7	163.2	165.2	162.5	165.2	155.6	143.9
6	96.1	93.8	110.9	96.3	96.5	96.0	104.8	106.0	104.8	108.8	115.5
7	166.8	165.7	166.7	166.3	169.6	166.8	161.7	165.2	161.7	159.2	157.4
8	95.1	93.1	101.0	95.1	95.5	94.9	95.1	95.6	95.1	102.6	109.6
9	162.5	161.7	163.6	162.8	163.3	162.3	161.3	159.0	161.2	160.5	159.8
10	100.6	103.7	112.0	100.5	100.9	100.3	101.0	104.5	101.0	100.0	105.9
1′	128.9	129.9	131.7	123.9	114.2	129.6	129.6	129.1	128.9	130.7	135.3
2′	115.3	112.5	104.7	154.2	159.0	147.8	115.6	110.6	107.8	128.7	126.9
3′	144.9	148.9	153.4	113.8	103.0	119.1	145.4	149.3	146.0	115.6	128.1
4′	145.7	149.5	138.8	153.4	157.5	115.0	146.2	149.3	133.9	156.3	129.5
5′	115.3	112.3	153.4	111.2	107.1	146.1	115.5	111.3	146.0	115.4	128.1
6′	119.2	120.6	104.7	128.1	130.3	111.6	120.6	120.4	107.8	128.7	126.9



1. 5-OH, 7-OH, 3′-OH, 4′-OH
2. 5-OCH_3, 7-OCH_3, 3′-OCH_3, 4′-OCH_3
3. 7-OCH_3, 3′-OCH_3, 4′-OCH_3, 5′-OCH_3
5. 5-OH, 7-OH, 2′-OH, 4′-OH
6. 5-OH, 7-OH, 2′-OH, 4′-OCH_3
7. 5-OH, 7-OH, 3′-OH, 4′-OH, 6-CH_3
8. 5-OCH_3, 7-OCH_3, 3′-OCH_3, 4′-OCH, 6-CH_3
9. 5-OH, 7-OH, 3′-OH, 4′-OH, 5′-OH, 6-CH_3



4



10. R = OH

11. R = H

第三节　异黄酮及二氢异黄酮类化合物的¹³C-NMR化学位移

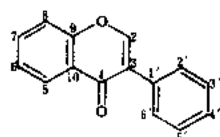
一、异黄酮类化合物的¹³C-NMR化学位移

表 22-13　异黄酮类化合物 1～12 的¹³C-NMR 化学位移数据[19,32,33]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
2	154.1	152.3	153.8	155.4	152.2	151.8	151.8	152.2	155.1	152.8	152.9	153.4
3	124.4	125.1	122.6	122.0	122.6	124.6	124.4	124.4	124.1	123.1	123.3	123.1
4	175.3	175.3	175.4	178.6	178.5	175.5	175.2	175.1	181.3	174.7	174.3	174.3
5	125.7	127.6	127.8	127.8	127.1	127.5	127.0	127.2	163.9	108.4	104.8	107.9
6	125.2	114.4	114.3	115.7	115.0	114.3	114.2	115.1	100.2	144.8	147.0	145.4
7	133.9	163.8	163.9	164.9	162.6	163.7	163.5	162.7	165.1	152.4	153.1	153.7
8	118.1	100.0	100.2	99.8	102.1	99.9	99.9	102.3	94.6	102.8	102.9	100.1
9	155.9	157.7	158.0	157.9	157.6	157.7	157.2	157.7	159.0	151.2	152.0	150.9
10	124.0	118.3	118.6	117.1	116.8	118.2	117.9	117.0	106.2	116.9	116.5	117.6

续表

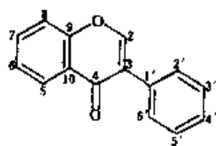
化合物 / C	1	2	3	4	5	6	7	8	9	10	11	12
1′	132.0	127.9	121.1	120.7	123.9	124.0	122.4	123.8	132.1	132.6	132.5	132.4
2′	128.2	128.2	157.6	156.6	129.9	129.6	129.7	130.0	129.9	128.9	128.9	128.9
3′	129.0	128.8	111.3	119.6	115.0	113.7	115.1	113.6	129.0	128.0	128.0	128.0
4′	127.9	131.7	131.8	130.5	147.3	159.3	157.5	159.2	128.9	127.5	127.5	127.6
5′	129.0	128.8	120.6	120.8	115.0	113.7	115.1	113.6	129.0	128.0	128.0	128.0
6′	128.2	128.2	129.7	129.7	129.9	129.9	129.7	130.0	129.0	128.9	128.9	128.9



1. —
2. 7-OCH_3
3. 7-OCH_3, 2′-OCH_3
4. 7-OCH_3, 2′-OH
5. 7-OH, 4′-OH
6. 7-OCH_3, 4′-OCH_3
7. 7-OCH_3, 4′-OH
8. 7-OH, 4′-OCH_3
9. 5-OH, 7-OH
10. 6-OH, 7-OH
11. 6-OCH_3, 7-OH
12. 6-OH, 7-OCH_3

表 22-14 异黄酮类化合物 13～24 的^{13}C-NMR 化学位移数据[5,32,33]

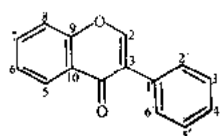
化合物 / C	13	14	15	16	17	18	19	20	21	22	23	24
2	153.2	153.7	153.6	153.6	154.4	154.0	150.6	154.3	151.9	152.3	152.0	152.2
3	123.6	123.7	123.6	121.4	123.3	122.6	125.0	122.5	123.2	122.7	123.4	123.4
4	174.3	174.9	174.9	180.2	181.5	180.5	174.3	180.0	174.8	174.6	174.7	174.8
5	104.3	121.0	106.1	157.6	163.9	162.1	161.0	162.3	108.4	108.3	104.8	108.1
6	147.5	110.7	154.9	98.6	99.9	98.0	96.1	99.2	144.6	144.6	146.9	145.2
7	154.3	156.3	128.0	164.3	165.0	165.4	163.8	164.5	152.2	152.2	152.9	153.5
8	100.0	136.3	120.8	93.7	94.5	92.2	92.8	93.8	102.8	102.7	102.9	99.8
9	151.9	150.2	149.5	157.6	159.0	157.7	159.1	157.7	151.3	151.1	152.0	151.0
10	117.2	118.8	126.4	104.6	106.2	105.7	109.3	104.7	116.9	116.8	116.5	117.7
1′	132.3	132.0	123.9	122.4	123.8	122.9	124.4	126.4	123.1	124.7	122.9	122.9
2′	128.9	128.9	130.0	130.0	131.0	130.1	130.2	106.6	130.0	130.0	130.0	130.0
3′	128.1	128.1	113.7	115.2	114.5	113.7	113.4	152.8	115.0	113.5	115.1	115.0
4′	127.6	127.8	159.3	162.1	161.7	159.4	159.5	137.7	157.2	158.9	157.3	157.3
5′	128.1	128.1	113.7	115.2	114.5	113.7	113.4	152.8	115.0	113.5	115.1	115.0
6′	128.9	128.9	130.0	130.0	131.0	130.1	130.2	106.6	130.0	130.0	130.0	130.0



13. 6-OCH_3, 7-OCH_3
14. 7-OCH_3, 8-OCH_3
15. 6-OCH_3, 4′-OCH_3
16. 5-OH, 7-OH, 4′-OH
17. 5-OH, 7-OH, 4′-OCH_3
18. 5-OH, 7-OCH_3, 4′-OCH_3
19. 5-OCH_3, 7-OCH_3, 4′-OCH_3
20. 5-OH, 7-OH, 3′-OCH_3, 4′-OCH_3, 5′-OCH_3
21. 6-OH, 7-OH, 4′-OH
22. 6-OH, 7-OH, 4′-OCH_3
23. 6-OCH_3, 7-OH, 4′-OH
24. 6-OH, 4-OH, 7-OH_3

表 22-15　异黄酮类化合物 25～38 的 ^{13}C-NMR 化学位移数据[3,32,33]

C \ 化合物	25	26	27	28	29	30	31	32	33	34	35	36	37	38
2	152.2	152.2	152.5	152.4	152.6	152.6	153.0	151.8	152.8	151.8	154.5	150.8	150.4	150.7
3	123.6	124.6	122.9	123.4	124.9	124.9	123.3	124.3	123.3	124.7	119.3	124.7	125.6	125.6
4	174.6	174.7	174.6	174.7	174.7	174.4	175.0	175.3	174.5	175.2	180.6	174.9	175.6	175.0
5	104.3	104.8	108.0	104.4	123.8	123.8	121.0	127.2	104.4	127.6	152.5	154.6	156.3	154.6
6	147.4	147.0	145.3	147.5	117.3	117.5	110.6	114.2	147.5	114.2	130.9	139.6	93.0	140.7
7	154.2	153.0	153.6	154.3	155.3	155.2	156.1	163.5	154.3	164.0	156.3	156.2	156.9	157.8
8	100.0	103.0	99.9	99.9	132.1	134.7	136.3	99.8	100.0	99.7	93.6	99.8	130.4	96.1
9	151.9	152.1	151.0	152.0	150.7	150.7	150.1	157.4	151.9	157.4	153.0	152.8	152.0	153.1
10	117.2	116.6	117.6	117.3	115.2	115.2	118.7	118.0	117.2	118.1	105.5	111.4	109.7	113.6
1′	122.7	123.1	124.6	124.4	125.1	126.0	124.0	124.4	124.9	125.5	110.4	126.0	125.7	125.7
2′	129.9	130.0	130.0	130.0	130.1	130.1	130.0	112.3	112.9	109.4	151.6	111.0	110.0	110.0
3′	115.0	113.5	113.5	113.6	113.6	113.6	113.6	148.4	148.8	147.4	97.8	147.4	147.5	147.6
4′	157.3	159.1	159.0	159.2	159.3	159.3	159.2	148.7	148.5	147.4	149.6	147.4	147.5	147.6
5′	115.0	113.5	113.5	113.6	113.6	113.6	113.6	110.9	111.5	108.0	142.4	108.1	108.1	108.3
6′	129.9	130.0	130.0	130.0	130.1	130.1	130.0	120.6	121.2	122.2	115.0	122.4	122.5	122.6



25. 6-OCH_3，7-OCH_3，4′-OH

26. 6-OCH_3，7-OH，4′-OCH_3

27. 6-OH，7-OCH_3，4′-OCH_3

28. 6-OCH_3，7-OCH_3，4′-OCH_3

29. 7-OH，8-OH，4′-OH

30. 7-OH，8-OH，4′-OCH_3

31. 7-OCH_3，8-OCH_3，4′-OCH_3

32. 7-OCH_3，3′-OCH_3，4′-OCH_3

33. 6-OCH_3，7-OCH_3，3′-OCH_3，4′-OCH_3，

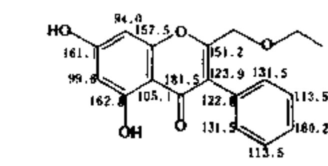
34. 7-OCH_3，3′，4′-（OCH_2O）-

35. 5-OH，7-OH，2′-OCH_3，4′-OCH_3，5′-OCH_3，6′-OCH_3

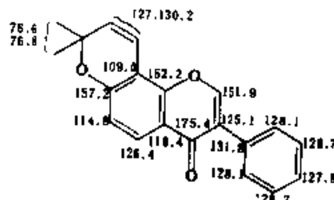
36. 5-OCH_3，6-OCH_3，7-OH，3′，4′-（OCH_2O）-

37. 5-OCH_3，7-OCH_3，5′-OCH_3，3′4′-（OCH_2O）-

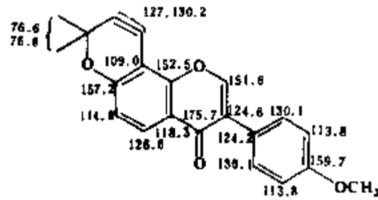
38. 5-OCH_3，6-OCH_3，7-OCH_3，3′，4′-（OCH_2O）-



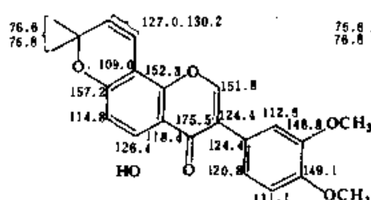
39[34]



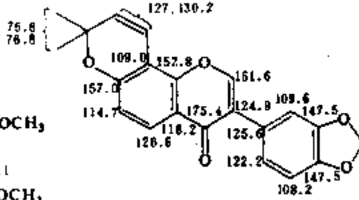
40[35]



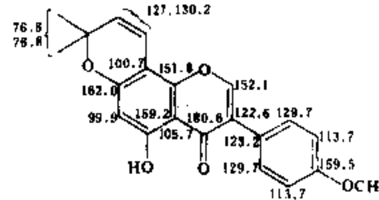
41[35]



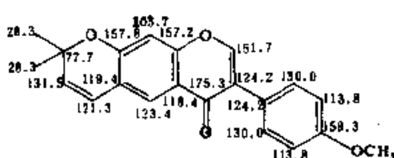
42[35]



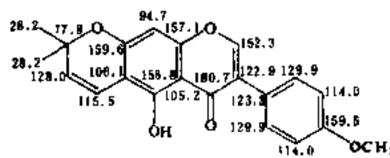
43[35]



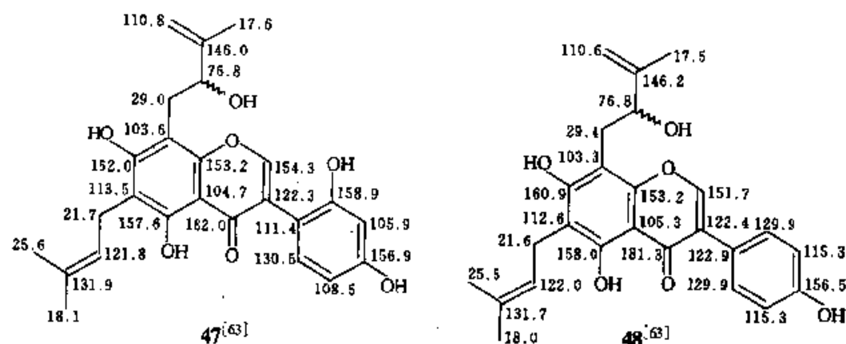
44[35]



45[35]

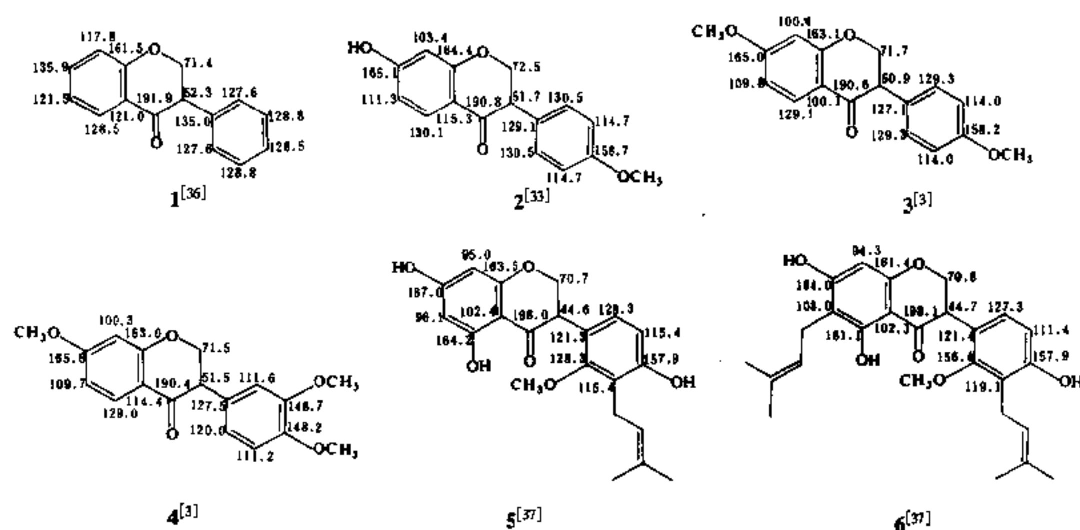


46[35]



47[63]　　48[63]

二、二氢异黄酮类化合物的^{13}C-NMR化学位移

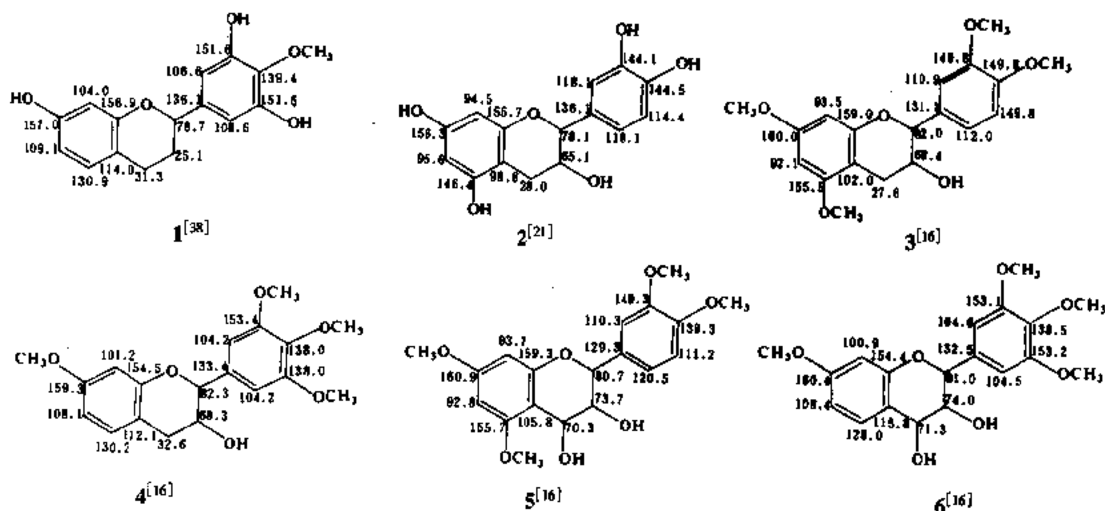


1[36]　　2[33]　　3[3]

4[3]　　5[37]　　6[37]

第三节　黄烷醇、查耳酮、橙酮类化合物的^{13}C-NMR化学位移

一、黄烷醇类化合物的^{13}C-NMR化学位移



1[38]　　2[21]　　3[16]

4[16]　　5[16]　　6[16]

7[21]

8[38]

9[39]

10[39]

二、异黄烷醇类化合物的13C-NMR化学位移

1[3]

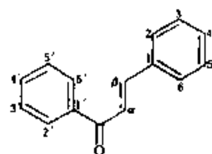
2[3]

3[3]

三、查耳酮类化合物的13C-NMR化学位移

表 22-16　查耳酮类化合物 1～12 的13C-NMR化学位移数据[19,21,40]

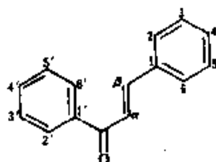
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
β	144.4	145.2	142.1	141.1	145.4	144.1	141.1	137.5	143.8	143.9	144.7	144.8
α	121.9	118.4	118.3	118.5	118.6	120.1	119.7	127.8	117.8	117.4	116.6	116.7
CO	190.0	193.5	194.9	194.3	193.7	191.5	192.8	191.1	191.1	191.4	191.7	191.7
1′	138.1	119.3	119.7	120.2	120.2	113.9	114.3	124.6	113.2	113.9	114.0	114.1
2′	130.3	163.5	163.4	163.6	163.6	166.5	166.5	160.4	164.6	160.3	165.7	166.3
3′	130.3	118.7	118.8	118.7	118.7	100.9	101.1	98.7	102.6	100.9	100.9	101.3
4′	132.6	136.2	136.0	136.1	136.1	166.0	166.0	164.0	165.4	165.7	166.2	165.9
5′	130.3	119.9	120.2	120.8	117.6	107.5	107.3	105.2	107.9	107.2	107.2	167.3
6′	130.3	129.6	129.8	129.7	129.5	131.0	131.5	132.8	132.3	130.9	131.0	131.2
1	134.9	138.4	121.8	123.7	127.4	134.6	132.0	122.6	125.8	127.2	126.0	126.1
2	128.7	128.9	157.9	159.1	130.5	128.8	157.7	158.7	130.6	130.1	130.4	130.6
3	128.7	128.5	116.7	111.3	114.5	128.3	116.7	111.2	115.8	114.2	116.1	116.2
4	128.4	130.8	132.1	132.2	162.1	130.4	131.8	131.2	159.9	161.5	160.1	160.3
5	128.7	128.5	120.1	120.8	114.5	128.3	120.4	120.7	115.8	114.2	116.1	116.2
6	128.7	128.9	130.0	129.6	130.5	128.8	129.9	128.7	130.6	130.1	130.4	130.6



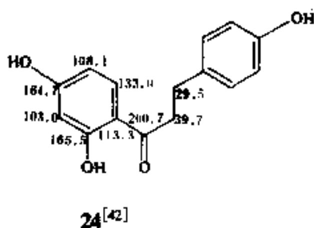
1. —
2. 2'-OH
3. 2-OH, 2'-OH
4. 2-OCH₃, 2'-OH
5. 4-OCH₃, 2'-OH
6. 2'-OH, 4'-OCH₃
7. 2-OH, 2'-OH, 4'-OCH₃
8. 2-OCH₃, 2'-OCH₃, 4'-OCH₃
9. 2-OH, 4-OH, 2'-OH
10. 4-OCH₃, 4'-OCH₃, 2'-OH
11. 4-OH, 2'-OCH₃, 4'-OCH₃
12. 4-OH, 2'-OH, 4'-OCH₃

表 22-17 查耳酮类化合物 13～23 的^{13}C-NMR 化学位移数据[6,19,20,41]

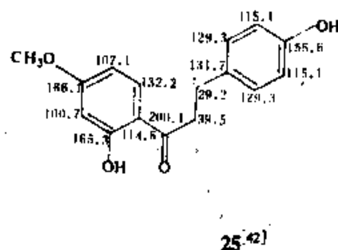
C \ 化合物	13	14	15	16	17	18	19	20	21	22	23
β	142.3	143.9	144.4	144.6	142.6	144.6	143.4	142.4	143.8	144.5	142.4
α	125.3	120.2	119.8	118.1	127.4	128.8	123.8	125.3	127.1	127.1	125.4
CO	190.2	191.3	191.6	191.7	193.2	193.2	192.5	192.6	193.8	194.6	192.3
1'	122.6	113.9	113.9	114.0	106.8	116.6	106.9	106.5	112.2	112.3	162.0
2'	161.6	166.4	166.3	166.0	158.6	153.3	157.1	162.6	158.8	157.4	93.9
3'	98.8	100.9	100.9	100.9	130.8	136.2	130.2	93.9	91.0	91.7	165.7
4'	164.4	105.9	165.9	165.8	159.4	155.0	157.4	168.5	162.4	160.2	91.1
5'	105.5	107.3	107.2	107.1	87.1	92.7	88.3	91.3	91.0	117.0	165.5
6'	132.9	131.0	131.3	131.9	158.5	151.8	156.0	166.1	158.8	156.3	106.3
1	128.4	135.9	135.8	127.7	135.4	134.8	125.6	128.5	127.7	127.8	128.5
2	130.2	113.2	135.0	114.9	128.9	128.8	130.5	130.1	130.0	130.2	130.2
3	114.6	159.7	157.6	146.9	128.3	128.4	115.9	114.4	114.4	114.4	116.6
4	160.6	116.1	118.1	156.4	130.1	130.3	160.3	161.5	161.5	161.6	159.3
5	114.6	129.7	129.7	111.6	128.3	128.4	130.5	114.4	114.4	114.4	116.6
6	130.2	120.9	120.0	122.1	128.9	128.8	115.9	130.1	130.0	130.2	130.2



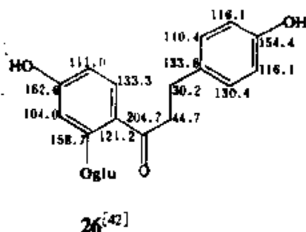
13. 4-OCH₃, 2'-OCH₃, 4'-OCH₃
14. 3-OCH₃, 2'-OH, 4'-OCH₃
15. 3-OH, 2'-OH, 4'-OCH₃
16. 3-OH, 4'-OCH₃, 2'-OCH₃, 4'-OCH₃
17. 2'-OCH₃, 4'-OCH₃, 5'-OCH₃, 6'-OH
18. 2'-OCH₃, 4'-OCH₃, 5'-OCH₃, 6'-OCH₃
19. 4-OH, 2'-OCH₂, 4'-OCH₃, 5'-OCH₃, 6'-OH
20. 4-OCH₃, 2'-OH, 4'-OCH₃, 6'-OCH₃
21. 4-OCH₃, 2'-OCH₃, 4'-OCH₃, 6'-OCH₃
22. 4-OCH₃, 2'-OCH₃, 3'-CH₃, 4'-OCH₃, 6'-OCH₃
23. 4-O-glu, 2'-OH, 4'-OCH₃, 6'-OCH₃



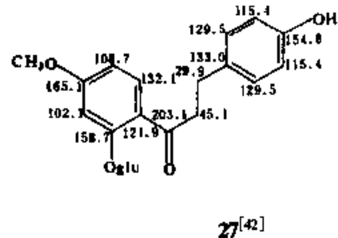
24[42]



25[42]



26[42]

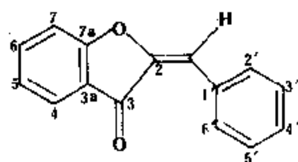


27[42]

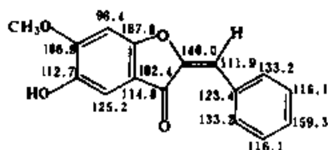
四、橙酮类化合物的^{13}C-NMR化学位移

表 22-18 橙酮类化合物 1～14 的^{13}C-NMR化学位移数据[19,43]

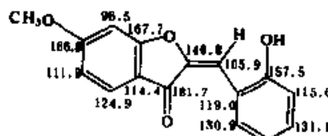
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
2	146.8	148.5	147.6	145.8	146.0	147.4	146.4	147.5	147.0	148.1	145.9	147.0	146.4	147.6
3	184.5	182.8	182.6	184.3	182.4	184.8	184.7	183.0	185.8	184.0	185.3	183.5	183.3	182.6
4	124.5	124.1	125.5	124.4	125.2	134.5	139.4	139.4	137.0	137.0	136.5	136.5	136.0	125.5
5	123.3	132.4	112.0	123.1	112.7	126.1	125.9	125.3	124.5	123.8	124.2	123.5	126.5	112.0
6	136.7	138.0	167.2	136.4	166.9	148.2	147.8	147.8	137.1	137.1	136.5	136.5	147.6	167.2
7	112.8	112.1	95.5	113.2	96.4	110.1	110.1	109.7	119.5	119.8	119.3	119.1	117.7	96.5
7a	166.0	163.8	168.3	165.7	167.8	166.8	166.6	165.9	164.8	164.2	164.4	163.7	165.0	168.3
3a	131.5	123.3	114.6	121.5	148.8	117.4	117.7	119.3	119.1	120.6	119.1	120.7	117.0	114.6
=CH	112.8	122.2	111.6	112.7	111.9	111.9	111.6	121.5	111.5	121.3	111.6	121.7	110.7	111.6
1′	132.2	131.9	132.2	124.9	123.4	132.6	125.3	125.0	132.7	132.0	125.3	125.0	132.8	132.2
2′	131.4	130.8	128.6	133.3	133.2	131.2	133.0	132.8	131.3	130.7	132.9	132.8	131.1	131.1
3′	128.8	128.4	131.1	114.4	116.1	128.7	134.3	113.8	128.8	128.3	114.2	113.6	128.7	128.6
4′	129.8	130.2	129.4	161.0	159.3	129.3	160.7	161.1	129.4	129.9	160.5	161.1	129.1	129.4
5′	128.8	128.4	131.1	114.4	116.4	128.7	114.3	113.8	128.8	128.3	114.2	113.6	128.7	128.6
6′	131.4	130.8	128.6	133.3	133.2	131.2	133.0	132.8	131.3	130.7	132.9	132.8	131.1	131.1



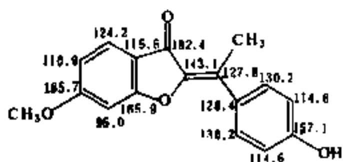
1.
2. 5-CH_3
3. 6-OCH_3
4. 4′-OCH_3
5. 6-OCH_3, 4′-OH
6. 4-CH_3, 6-CH_3
7. 4-CH_3, 6-CH_3, 4-OCH_3 (*Z*)
8. 4-CH_3, 6-CH_3, 4′-OCH_3 (*E*)
9. 4-CH_3, 7-CH_3 (*Z*)
10. 4-CH_3, 7-CH_3 (*E*)
11. 4-CH_3, 7-CH_3, 4′-OCH_3 (*Z*)
12. 4-CH_3, 7-CH_3, 4′-OCH_3 (*E*)
13. 4-CH_3, 6-CH_3, 7-CH_3
14. 6-OCH_3



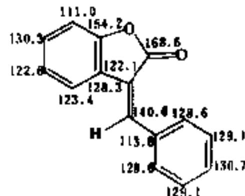
15[43]



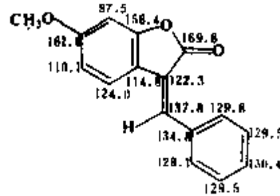
16[43]



17[43]



18[19]

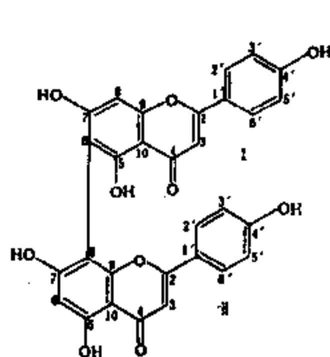


19[19]

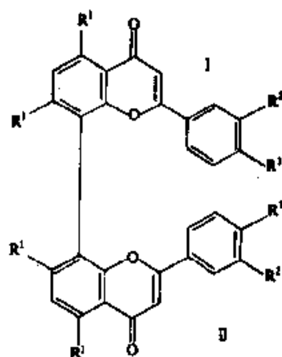
第四节 双黄酮类化合物的^{13}C-NMR化学位移

表 22-19 双黄酮类化合物 1～6 的^{13}C-NMR化学位移数据[44,45]

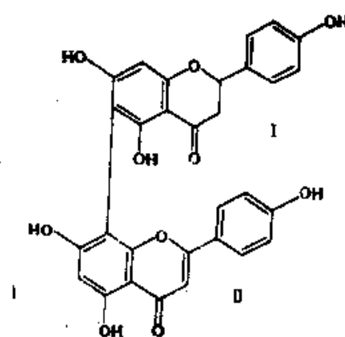
结构部分	化合物 / C	1	2	3	4	5	6
I	2	164.1	163.9	161.0	78.7	78.5	78.6
	3	103.1	102.8	106.0	42.2	42.2	42.3
	4	182.3	182.1	177.7	196.5	196.3	196.4
	5	160.0	161.3	161.6	161.8	161.8	161.8
	6	103.6	99.0	91.6	100.3	101.1	101.2
	7	162.9	162.7	164.8	165.2	165.3	165.2
	8	93.7	98.7	102.0	94.8	94.7	94.6
	9	157.0	155.3	160.4	162.4	161.9	162.7
	10	103.8	104.3	107.7	101.9	101.9	107.8
	1′	121.5	121.7	123.4	129.1	129.3	129.2
	2′	128.6	127.9	107.7	128.2	128.3	128.1
	3′	116.2	116.1	148.8	115.5	115.4	115.4
	4′	161.3	161.1	151.4	157.9	157.8	157.7
	5′	116.2	116.1	111.0	115.5	115.4	115.4
	6′	128.6	127.9	118.9	128.2	128.3	128.1
II	2	163.9	163.9	161.0	163.8	78.5	77.9
	3	102.8	102.8	106.0	102.8	42.2	42.1
	4	182.1	182.1	177.7	182.3	196.3	196.3
	5	160.9	161.3	161.6	160.7	161.9	161.8
	6	98.9	99.0	91.6	98.8	101.1	95.7
	7	162.7	162.7	164.8	162.8	165.3	165.2
	8	99.4	98.7	102.0	99.5	94.7	100.3
	9	155.1	155.3	160.4	151.9	161.9	161.6
	10	104.0	104.3	107.7	103.9	101.9	102.1
	1′	121.7	121.7	123.4	121.7	129.3	129.2
	2′	128.2	127.9	107.7	128.4	128.3	127.6
	3′	116.2	116.1	148.8	116.2	115.4	115.3
	4′	161.2	161.1	151.4	161.2	157.8	157.3
	5′	116.2	116.1	111.0	116.2	115.4	115.3
	6′	128.2	127.9	118.9	128.4	128.3	128.1



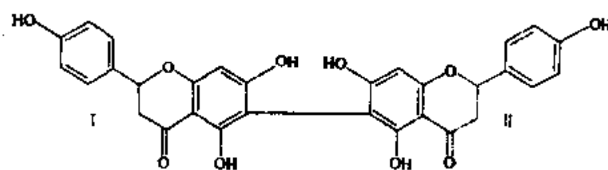
1



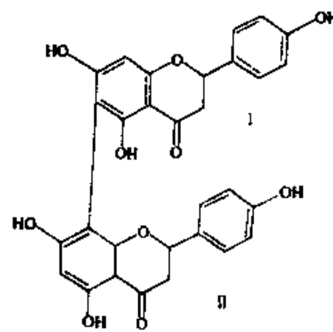
2. R^1 = OH, R^2 = H
3. R^1 = R^2 = OCH_3



4



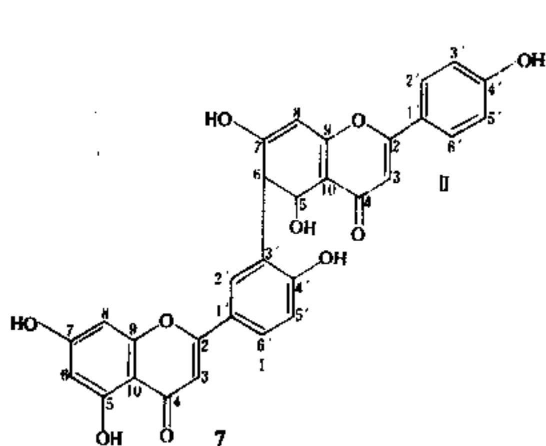
5

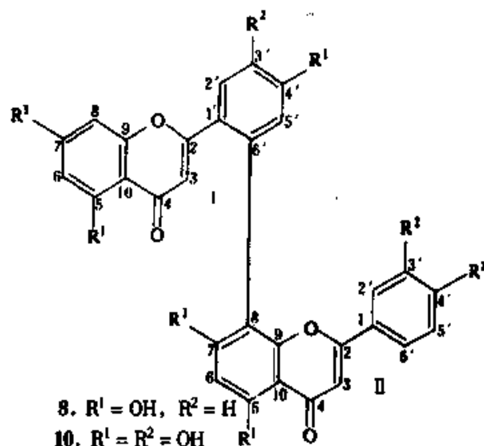


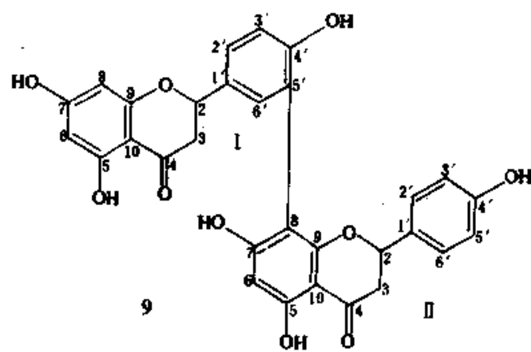
6

表 22-20 双黄酮类化合物 7～13 的 ^{13}C-NMR 化学位移数据[44～47]

结构部分	化合物 / C	7	8	9	10	11	12	13
I	2	164.1	164.0	78.7	164.4	82.7	79.6	82.6
	3	102.9	103.2	42.3	103.3	47.3	45.2	48.9
	4	181.7	181.8	196.7	182.3	197.4	195.4	197.7
	5	161.5	160.6	163.6	162.1	163.7		161.5
	6	99.0	98.9	95.8	99.3	96.1	94.0	95.6
	7	163.7	163.9	166.7	164.4	164.6		165.2
	8	94.0	94.2	95.1	94.3	95.0	93.0	95.6
	9	157.5	157.6	157.1	157.7	162.7		164.9
	10	103.9	104.0	102.1	104.2	101.3	99.2	102.4
	1′	121.4	121.3	131.2	121.4	129.8	126.1	129.4
	2′	127.2	127.9	128.3	112.7	127.7	126.9	115.4
	3′	120.8	121.6	115.1	145.9	114.8	112.8	145.0
	4′	159.7	159.6	160.2	148.6	157.7	155.7	145.1
	5′	116.7	116.4	120.1	120.6	114.8	112.8	115.4
	6′	131.0	131.6	126.9	122.7	126.7	128.9	120.2
II	2	164.1	164.3	77.9	164.4	82.7	80.8	84.0
	3	102.9	102.8	41.6	103.3	70.0	70.0	73.1
	4	181.8	182.2	196.2	181.9	196.5	194.5	197.7
	5	160.0	160.8	162.5	161.0	163.7		161.5
	6	103.5	99.1	95.7	99.3	96.1	93.0	96.8
	7	163.1	162.0	164.7	161.8	164.6		166.7
	8	93.9	104.1	105.9	104.2	101.1		102.6
	9	156.6	154.7	155.9	155.0	162.1		163.9
	10	103.9	104.0	101.1	104.2	101.1	99.2	102.4
	1′	121.6	120.3	129.1	122.4	128.8	125.9	129.4
	2′	128.3	128.3	127.8	114.1	111.8	112.8	115.7
	3′	116.1	116.0	115.1	146.2	146.2	142.8	145.0
	4′	161.1	116.0	163.1	149.8	146.2	143.8	149.7
	5′	116.1	116.6	115.1	116.1	114.8	112.8	115.7
	6′	128.3	128.3	127.8	119.1	128.8	126.9	120.2







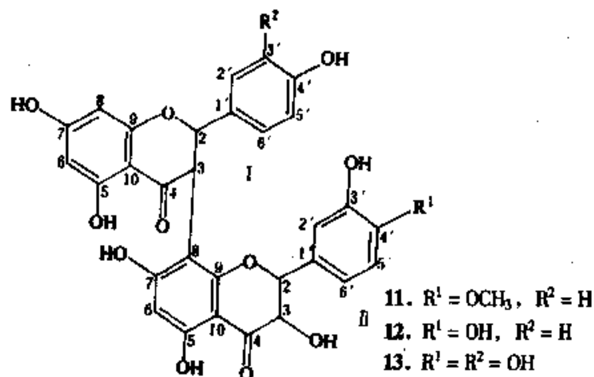
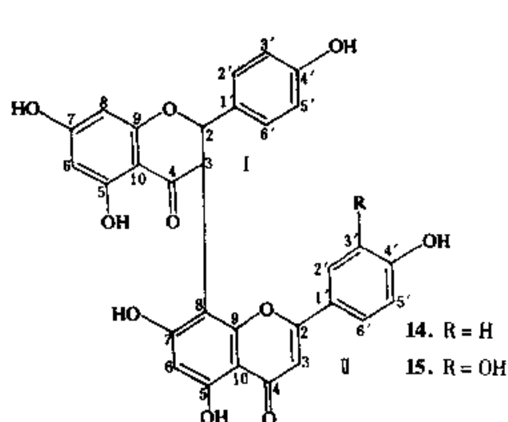
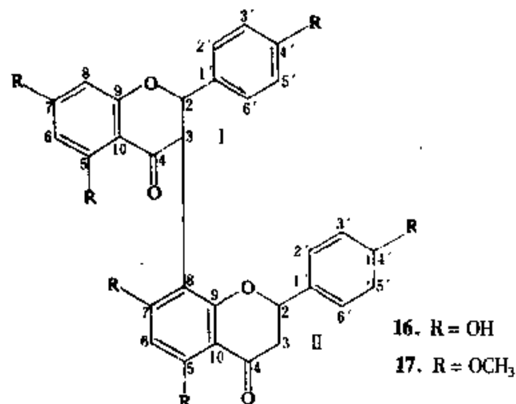
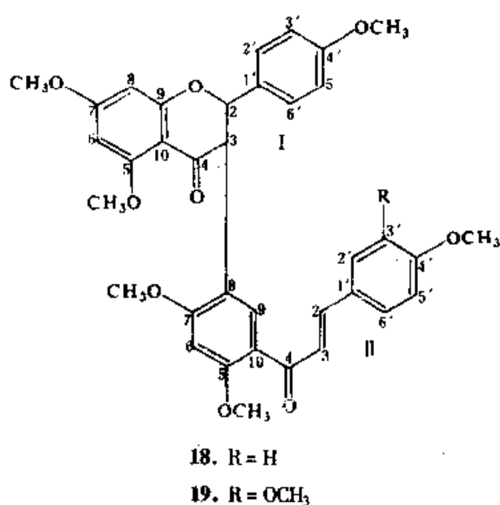


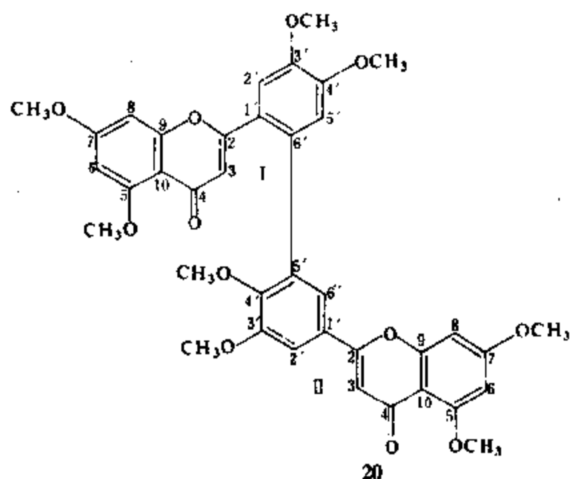
表 22-21　双黄酮类化合物 14 ~ 20 的 ^{13}C-NMR 化学位移数据[44,45,48]

结构部分	C ＼ 化合物	14	15	16	17	18	19	20
Ⅰ	2	81.4	81.0	81.4	82.1	81.7	81.6	160.6
	3	48.2	48.7	47.7	48.8	51.0	51.1	108.5
	4	196.0	195.6	195.2	197.2	193.7	193.4	177.3
	5	163.4	163.5	163.4	164.4	164.9	164.5	160.0
	6	96.4	96.2	96.0	95.3	93.1	93.4	92.7
	7	166.6	166.3	165.9	167.7	162.1	165.0	163.8
	8	95.3	95.2	95.0	94.1	105.8	93.0	96.2
	9	163.7	162.5	162.3	163.0	130.3	162.0	159.6
	10	101.7	101.5	101.3	103.2	128.2	105.7	109.0
	1′	128.1	128.0	127.9	130.2	113.2	130.3	126.5
	2′	128.1	128.1	128.5	128.6	159.1	128.1	109.3
	3′	114.6	114.4	114.5	113.5	113.2	113.1	149.5
	4′	162.0	157.1	157.1	159.9	159.1	159.1	152.9
	5′	114.6	114.4	114.5	113.5	113.2	113.1	132.2
	6′	128.1	128.1	128.5	128.6	128.2	128.1	120.9
Ⅱ	2	163.7	163.2	78.3	79.1	144.4	144.6	160.6
	3	102.8	102.8	43.0	46.1	126.4	126.6	108.5
	4	181.6	181.4	196.1	189.5	189.3	180.2	177.3
	5	160.4	160.3	162.3	164.4	157.5	157.3	160.0
	6	98.5	98.6	94.9	89.2	91.5	91.6	92.7
	7	162.8	161.4	164.3	167.7	159.0	159.1	163.8
	8	100.6	100.2	101.3	102.9	115.4	115.4	96.2
	9	157.3	155.0	162.0	162.0	157.1	157.1	159.6
	10	103.7	103.2	101.0	106.0	110.5	110.5	109.0
	1′	121.3	131.1	128.9	130.9	127.2	127.3	126.5
	2′	128.1	131.1	127.3	127.8	129.2	109.9	109.3
	3′	115.9	145.4	114.9	114.1	113.9	148.8	149.5
	4′	161.0	149.4	157.1	159.9	161.0	150.9	152.9
	5′	115.9	116.1	114.9	114.1	113.9	110.9	132.2
	6′	128.1	119.0	127.3	127.8	129.2	122.8	120.9



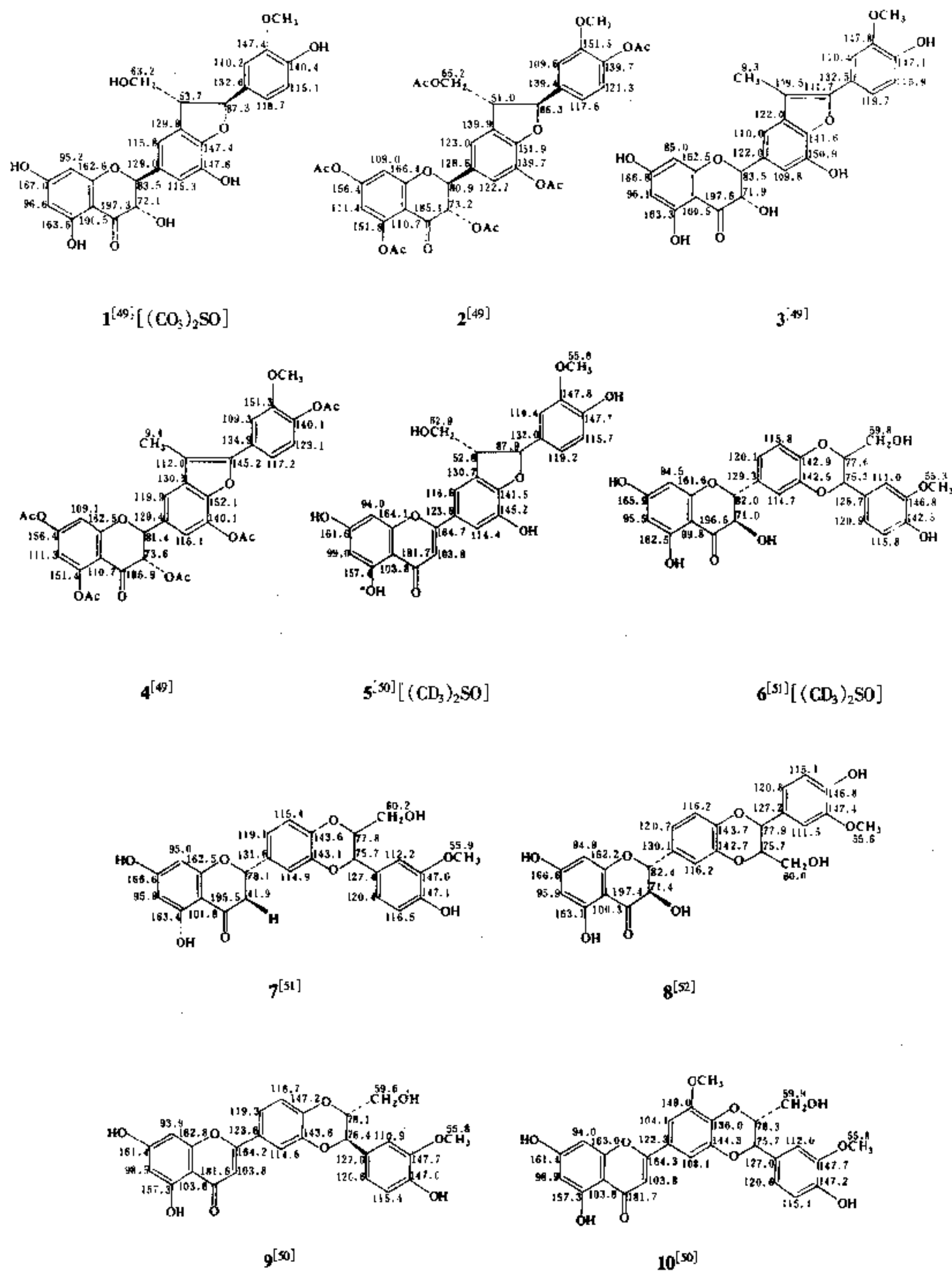






第五节 黄酮木脂素及黄酮甙类化合物的^{13}C-NMR 化学位移

一、黄酮木脂素类化合物的^{13}C-NMR 化学位移

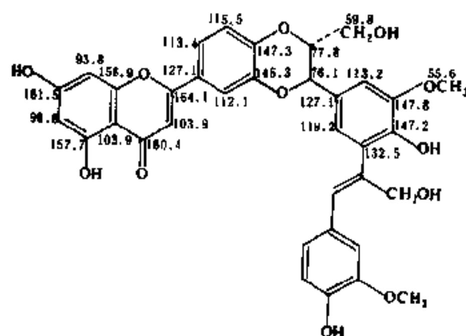


1[49][$(CD_3)_2SO$]　2[49]　3[49]

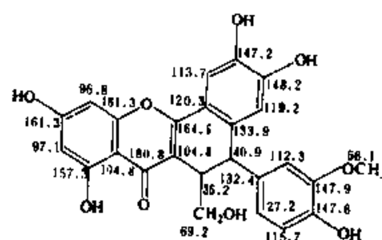
4[49]　5[50][$(CD_3)_2SO$]　6[51][$(CD_3)_2SO$]

7[51]　8[52]

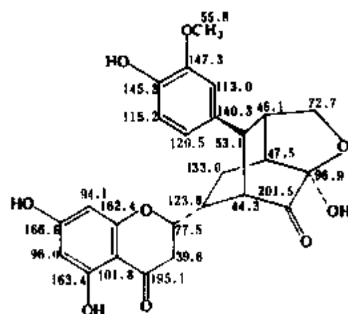
9[50]　10[50]



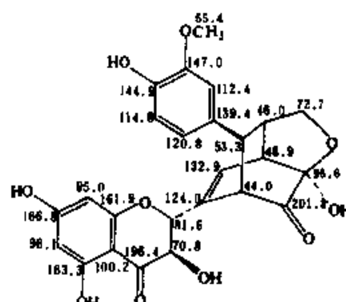
11[50][$(CD_3)_2SO$]



12[50][$(CD_3)_2SO$]



13[51][$(CD_3)_2SO$]



14[51][$(CD_3)_2SO$]

二、黄酮甙类化合物的^{13}C-NMR化学位移

表 22-22　黄酮甙类化合物 1～12 的^{13}C-NMR 化学位移数据[5,7,54-57]①

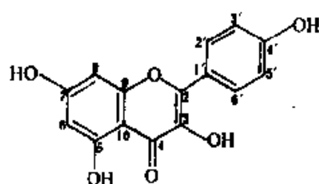
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
2	163.3	164.2	164.4	162.8	164.1	164.0	163.8	163.9	163.2	163.8	163.2	164.4
3	103.3	103.3	103.1	103.2	103.7	102.6	102.9	102.6	102.1	102.4	101.9	103.4
4	182.3	181.9	181.9	182.0	181.4	181.9	181.9	182.2	181.9	182.0	181.7	182.3
5	157.2	161.3	162.0	157.0	161.2	155.8	156.9	155.0	160.8	160.9	154.4	156.7
6	99.7	98.8	99.1	99.7	99.0	98.9	108.8	107.6	108.1	108.0	108.3	110.7
7	164.6	162.8	162.4	164.3	162.6	162.5	163.8	161.4	161.1	161.7	160.7	162.6
8	95.1	95.0	94.8	94.9	94.0	104.2	94.2	103.7	103.9	104.4	104.2	94.0
9	161.9	157.0	157.0	161.4	157.1	160.6	161.3	161.3	154.0	154.8	158.0	161.5
10	105.6	105.6	105.5	105.5	104.0	104.2	103.5	105.3	103.3	102.9	103.8	105.2
1′	121.1	121.3	120.6	121.1	124.4	121.8	121.2	121.5	121.1	121.4	121.4	121.1
2′	128.8	128.5	128.6	128.5	128.1	128.5	128.4	129.0	128.6	128.5	128.5	128.8
3′	116.3	116.1	116.3	116.0	116.5	116.0	116.3	115.9	115.7	115.7	116.8	116.3
4′	161.3	161.2	161.2	161.2	159.1	160.9	160.6	158.7	159.2	158.4	160.7	159.6
5′	116.3	116.1	116.3	116.0	128.1	116.0	116.3	115.9	115.7	115.7	116.0	120.5
6′	128.8	128.5	128.6	128.5	116.6	128.5	128.4	129.0	128.6	128.5	128.5	127.7

① 以[$(CD_3)_2SO$]作溶剂。

表 22-23 黄酮甙类化合物 1～12 糖部分的^{13}C-NMR 化学位移数据[5,7,54-57]①

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
1″	101.5	99.7	100.8	99.8	97.2	80.9	79.0	80.8	73.3	73.3		80.5
2″	74.0	76.8	75.7	73.1	74.0	75.1	73.4	76.0	70.5	70.7		74.4
3″	76.1	76.6	75.7	76.3	73.0	73.0	70.7	72.2	78.4	78.9		72.0
4″	71.2	70.2	70.7	70.0	70.1	72.0	70.7	71.7	70.0	70.5		71.9
5″	77.4	77.2	77.1	74.0	73.7	81.8	81.3	81.4	81.0	82.0		82.7
6″	61.0	60.9	59.7	63.5	63.4	62.6	61.6	61.7	60.7	61.4		60.6
1‴		109.0	100.5，97.6	170.2				81.2	74.8	74.3		100.0
2‴		76.5	70.5；70.5	20.5				76.0	74.3	74.0		73.1
3‴		79.1	70.7，70.7					73.0	70.8	70.9		78.9
4‴		74.0	72.0，72.0					72.0	68.9	69.6		71.3
5‴		64.4	68.5，68.5					82.6	68.5	68.6		77.3
6‴			18.2，17.9					62.8				62.0

① 以[$(CD_3)_2SO$]为溶剂。



1. 7-glu
2. 7-glu-（2-1）-Api
3. 7-glu-（2″，4″）-rha
4. 3-（6″-Ac）glu
5. 4′-（2″，6″-香豆酰基）glu
6. 8-glu
7. 6-glu
8. 6，8-glu
9. 6-glu-8-ara
10. 6-ara-8-glu
11. 6-gal-8-ara
12. 6-C，7-*O*-glu

表 22-24 黄酮甙类化合物 13～25 的^{13}C-NMR 化学位移数据[53]①

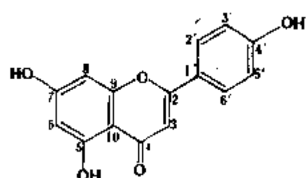
C \ 化合物	13	14	15	16	17	18	19	20	21	22	23	24	25
2	156.3	156.4	156.6	147.9	156.1	156.0	155.8	155.9	156.0	156.0	156.0	147.9	156.0
3	133.0	133.1	133.5	135.9	133.8	133.6	133.4	133.3	133.8	133.6	133.7	136.0	133.7
4	177.4	177.5	177.5	176.1	177.7	177.5	177.4	177.5	177.6	177.5	177.6	176.1	177.6
5	161.1	161.2	161.3	160.4	160.9	160.8	160.8	160.9	160.9	160.9	160.9	160.5	160.9
6	98.7	98.6	98.8	98.8	99.6	99.5	99.4	99.4	99.4	99.5	99.4	99.2	99.7
7	164.1	164.0	164.2	162.4	163.0	162.9	162.8	162.8	161.8	161.8	161.7	162.9	162.9
8	93.6	93.6	93.8	94.4	94.8	94.7	94.5	44.6	94.5	94.6	94.6	94.8	94.9
9	156.3	156.4	156.9	155.9	157.0	157.1	155.8	155.9	156.8	157.2	157.1	156.0	157.2
10	104.1	104.2	104.2	104.9	105.9	105.7	105.9	105.8	105.8	105.7	105.8	105.0	105.8
1′	121.0	121.1	121.1	121.6	120.9	120.7	121.0	120.8	120.9	120.7	120.8	121.7	120.8
2′	130.7	130.6	130.9	129.5	130.9	130.6	130.6	130.7	130.7	130.7	130.7	129.6	130.7
3′	115.0	115.2	115.2	115.5	115.2	115.0	115.1	115.2	115.0	115.0	115.1	115.6	115.7
4′	159.8	159.7	159.9	159.4	160.1	160.0	159.9	159.9	160.0	160.1	159.9	159.4	159.9
5′	115.0	115.2	115.2	115.5	115.2	115.0	115.1	115.2	115.0	115.1	115.1	115.6	115.7
6′	130.7	130.6	130.9	129.5	130.9	130.6	130.6	130.7	130.7	130.7	130.7	129.6	130.7

① 以[$(CD_3)_2SO$]为溶剂。

表 22-25 黄酮甙类化合物 13～25 糖部分的^{13}C-NMR 化学位移数据[53]①

糖	C \ 化合物	13	14		15	16	17		18		19		
葡萄糖	1	101.4	98.6	103.6	101.5	98.4	100.3	101.3	100.3	101.3	100.4	97.7	99.1
	2	74.2	82.0	74.3	74.2	77.3	73.3	74.4	73.2	74.1	73.2	80.0	74.6
	3	76.5	76.6	76.7	76.5	77.1	76.6	76.6	76.5	76.4	76.7	76.7	74.1
	4	70.1	70.0	70.5	70.1	70.1	70.0	70.2	70.0	70.0	70.0	70.4	70.7
	5	77.2	76.6	76.7	75.8	76.8	77.3	77.4	77.1	74.1	77.0	77.0	76.1
	6	61.0	61.0	61.4	66.9	60.9	61.0	61.0	60.9	62.8	61.2	61.0	61.0
鼠李糖	1				100.6	100.5							
	2				70.3	70.5							
	3				70.7	70.8							
	4				72.0	72.2							
	5				68.1	68.3							
	6				17.4	20.9							
糖	C \ 化合物	20			21	22	23			24	25		
葡萄糖	1	100.3	98.4	103.6	101.5	101.3		101.4		100.5	100.7	101.4	
	2	73.2	82.1	74.3	74.3	74.1		74.2		78.4	73.2	74.2	
	3	76.4	76.6	76.6	76.5	76.4		76.6		76.7	76.6	76.6	
	4	69.9	69.9	70.3	70.0	70.0		70.2		70.1	70.0	70.2	
	5	77.2	77.2	76.6	77.1	74.1		76.0		77.3	77.2	76.0	
	6	60.9	61.0	61.3	61.1	62.9		66.9		61.2	61.6	67.0	
鼠李糖	1				98.9	98.7	98.9		100.6			100.3	
	2				70.3	70.0	70.0		70.3			70.4	
	3				70.6	70.5	70.6		70.8			70.8	
	4				71.8	71.8	71.9		72.1			72.1	
	5				70.0	69.8	69.8		68.1			68.1	
	6				17.5	17.7	17.5		17.5			17.5	

① 以[$(CD_3)_2SO$]为溶剂。



13. 3-*O*-glu
14. 3-*O*-glu (2-1) glu
15. 3-*O*-glu (6-1) rha
16. 7-*O*-glu (6-1) rha
17. 7-*O*-glu 3-*O*-glu
18. 7-*O*-glu 3-*O*-glu (*O*-Ac)
19. 7-*O*-glu3-*O*-glu (2-1) glu (*O*-芥子酰基)
20. 7-*O*-glu 3-*O*-glu (2-1) glu
21. 7-*O*-rha 3-*O*-glu
22. 7-*O*-rha 3-*O*-glu (OAc)
23. 7-*O*-rha 3-*O*-glu (6-1) rha
24. 7-*O*-glu
25. 7-*O*-glu 3-*O*-glu (6-1) rha

表 22-26 黄酮甙类化合物 26～35 的^{13}C-NMR 化学位移数据[53]①

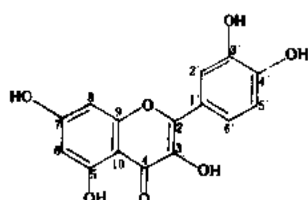
C \ 化合物	26	27	28	29	30	31	32	33	34	35
2	156.5	156.3	156.3	156.4	156.4	147.0	156.2	156.2	147.3	147.9
3	133.7	133.8	133.7	133.5	134.4	136.5	133.4	133.3	136.3	135.9
4	177.6	177.5	177.4	177.8	177.7	176.3	177.5	177.3	176.1	175.9
5	161.3	161.2	161.2	161.2	161.2	161.0	161.3	161.2	160.4	160.3
6	98.8	98.6	98.8	98.7	98.6	98.7	98.8	98.7	98.9	98.9
7	164.2	164.0	164.1	164.1	164.0	164.3	164.2	164.0	162.8	162.7
8	93.6	93.4	93.6	93.5	93.5	93.9	93.7	93.7	94.5	94.5
9	156.5	156.3	156.5	156.8	157.0	156.7	156.4	156.4	155.8	155.7
10	104.2	104.0	104.0	104.1	104.2	103.5	104.2	104.1	104.8	104.7
1'	121.4	121.3	121.2	121.1	121.0	125.8	121.2	121.2	123.4	121.9
2'	115.3	115.2	115.2	115.6	115.4	115.7	113.9	113.9	115.2	115.5
3'	144.8	144.7	144.7	145.0	145.1	147.0	149.5	149.5	146.3	145.0
4'	148.5	148.3	148.4	148.4	148.3	146.4	147.1	147.0	149.6	147.9
5'	116.5	116.2	116.2	115.8	115.8	117.0	115.3	115.3	112.4	115.4
6'	121.6	121.8	121.8	121.6	121.0	120.0	122.1	122.4	119.9	120.1

① 以[$(CD_3)_2SO + D_2O$]作溶剂。

表 22-27　黄酮甙类化合物 26～35 糖部分的13C-NMR 化学位移数据[53]①

糖	C＼化合物	26	27	28	29		30	31	32	33	34	35
葡萄糖	1	101.4						102.2		101.5	100.3	100.3
	2	74.3						73.7		74.4	73.2	73.2
	3	76.8						76.4		76.7	76.4	76.5
	4	70.3						70.5		70.2	69.8	69.9
	5	77.5						77.5		76.1	75.8	77.2
	6	61.3						61.4		67.0	66.2	60.9
鼠李糖	1						101.9				100.5	
	2						70.4				70.3	
	3						70.6				70.9	
	4						71.5				72.2	
	5						70.1				68.4	
	6						17.3				17.6	
其他糖	1		102.3	102.4	108.1	101.8			102.0			
	2		71.3	71.2	82.1	71.7			71.5			
	3		73.4	73.1	77.2	70.8			73.4			
	4		68.0	68.0	86.2	65.9			68.1			
	5		75.8	72.7	61.0	64.1			75.9			
	6		60.8	62.3					60.4			

① 以[$(CD_3)_2SO$]作溶剂。



26. 3-*O*-glu
27. 3-*O*-gal
28. 3-*O*-gal [6″-*O*-(3, 4, 5-三羟基苯甲酰)]
29. 3-*O*-ara
30. 3-*O*-rha
31. 4′-*O*-glu
32. 3′-OCH_3, 3-*O*-gal
33. 3′-OCH_3, 3-*O*-glu 6-1 rha
34. 4′-OCH_3, 7-*O*-glu 6-1 rha
35. 7-*O*-glu

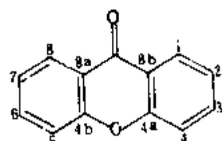
第六节　吅酮、色酮类化合物的13C-NMR 化学位移

一、吅酮类化合物的13C-NMR 化学位移

表 22-28　吅酮类化合物 1～9 的13C-NMR 化学位移数据[58]①

C＼化合物	1	2	3	4	5	6	7	8	9
1	125.92	160.98	108.58	127.96	115.25	162.91	162.93	162.88	162.81
2	124.28	110.16	153.91	114.08	124.12	98.16	98.14	97.99	97.87
3	135.44	137.45	124.47	164.01	120.21	165.90	165.78	165.16	165.61
4	118.10	107.18	119.35	102.16	146.64	94.10	94.09	93.96	93.76
4a	155.55	155.74	149.19	157.57	145.23	157.39	157.28	157.42	157.53
4b	155.55	155.61	155.54	155.57	155.38	155.35	144.88	157.42	149.03
5	118.10	117.98	118.03	117.81	118.23	117.61	146.15	102.07	118.90
6	135.44	136.39	135.04	134.68	135.23	135.52	120.61	164.23	124.43
7	124.28	124.53	123.84	124.03	123.95	124.28	124.06	113.98	153.94
8	125.92	125.36	125.84	125.83	125.94	125.18	114.60	127.16	108.05
8a	121.12	119.83	120.45	121.25	120.94	119.84	120.95	112.28	120.43
8b	121.12	108.28	121.73	114.08	122.28	102.25	102.20	101.69	101.98
C=O	175.91	181.69	175.83	174.74	176.16	179.73	180.17	179.10	179.72

① 以[$(CD_3)_2SO$]作溶剂。

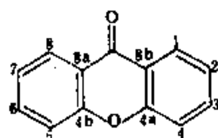


1. —
2. 1-OH
3. 2-OH
4. 3-OH
5. 4-OH
6. 1-OH, 3-OH
7. 1- OH, 3-OH, 5-OH
8. 1-OH, 3-OH, 6-OH
9. 1-OH, 3-OH, 7-OH

表 22-29 屾酮类化合物 10～15 的^{13}C-NMR 化学位移数据[58]①

C \ 化合物	10	11	12	13	14	15	C \ 化合物	10	11	12	13	14	15
1	162.18	162.94	162.66	161.94	161.89	161.86	8a	106.87	113.09	111.89	107.38	107.35	111.85
2	98.56	97.89	97.73	97.17	97.25	107.68	8b	101.14	101.48	101.65	101.76	101.98	101.43
3	166.55	165.14	164.71	167.09	166.94	163.89	C═O	183.41	179.69	179.94	184.26	183.91	179.20
4	94.35	93.95	93.64	92.75	92.78	93.48	1′						81.61
4a	157.44	157.38	157.39	157.71	157.22	156.33	2′						73.24
4b	155.47	146.10	150.98	148.01	143.29	150.89	3′						70.72
5	107.02	132.48	102.72	106.01	137.32	102.73	4′						70.45
6	137.13	151.92	154.03	124.21	123.73	154.11	5′						79.07
7	110.54	113.09	143.75	140.56	109.35	143.80	6′						61.61
8	160.29	115.93	108.16	147.11	151.83	108.21							

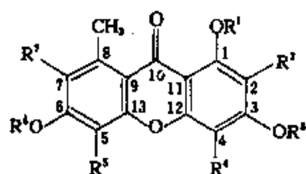
① 以[$(CD_3)_2SO$]作溶剂。



10. 1-OH, 3-OH, 8-OH
11. 1-OH, 3-OH, 5-OH, 6-OH
12. 1-OH, 3-OH, 6-OH, 7-OH
13. 1-OH, 3-OCH_3, 7-OH, 8-OH
14. 1-OH, 3-OCH_3, 5-OH, 8-OH
15. 1-OH, 2-β-D-glu, 3-OH, 6-OH, 7-OH

表 22-30 屾酮类化合物 16～24 的^{13}C-NMR 化学位移数据[59]

C \ 化合物	16	17	18	19	20	21	22	23	24
1	147.6	157.2	157.0	157.6	164.2	156.9	155.8	145.8	
2	114.1	114.5	119.9	120.5	92.3	108.3	115.7	116.1	
3	159.5	159.7	155.9	155.9	162.6	154.4	157.0	149.0	157.6
4	97.9	96.2	115.6	115.2	95.0	112.7	115.4	116.3	
5	107.0	106.7	98.4	108.0	98.0	108.4	113.6	120.3	
6	158.3	158.0	163.5	158.9	158.1	153.9	158.0	149.5	151.3
7	111.2	110.7	116.1	111.6	115.1	120.8	127.5	127.0	122.4
8	142.0	141.8	143.7	141.7	143.8	144.1	138.8	139.2	141.5
9	115.4	115.8	114.9	115.7	115.5	118.6	121.0	119.9	
10	174.9	175.6	175.2	175.2	177.1	176.1	175.2	174.5	174.9
11	110.2	111.6	112.7	113.5	108.0	113.7	118.9	115.3	
12	155.5	156.0	151.5	151.6	162.0	157.4	151.4	151.4	
13	153.2	153.0	158.1	153.2	159.0	151.1	150.5	150.5	
14	23.5	23.9	23.4	23.7	23.8	23.3	18.2	18.3	23.1
1-OCH_3		61.6	61.1	61.2	55.5		61.0		
3-OCH_3	56.5	56.6	61.8	61.9	55.6		61.3		61.4
6-OCH_3	56.9	56.8	55.7	56.6	56.3		62.1		
OAc	20.8					21.9		20.1	20.6
								20.2	20.8
								20.7	
	168.5					167.9		165.9	
						168.4		166.3	
						169.4		167.7	



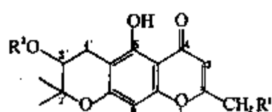
化合物 \ 取代基	R¹	R²	R³	R⁴	R⁵	R⁶	R⁷
16	Ac	Cl	CH_3	H	Cl	CH_3	H
17	CH_3	Cl	CH_3	H	H	CH_3	H
18	CH_3	Cl	CH_3	Cl	H	CH_3	H
19	CH_3	Cl	CH_3	Cl	Cl	CH_3	H
20	CH_3	H	CH_3	H	H	CH_3	H
21	Ac	H	Ac	H	H	Ac	H
22	CH_3	Cl	CH_3	Cl	Cl	CH_3	Cl
23	Ac	Cl	Ac	Cl	Cl	Ac	Cl
24	Ac	Cl	CH_3	Cl	Cl	Ac	H

二、色原酮类化合物的^{13}C-NMR化学位移

表 22-31　色原酮类化合物 25 ~ 29 的^{13}C-NMR 化学位移数据

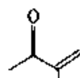
C \ 化合物	25	26	27	28	29①	C \ 化合物	25	26	27	28	29①
2	166.9	166.8	166.8	168.4	167.4	CH_3	25.0	24.7	24.9	24.9	25.7
3	108.4	108.4	108.4	106.2	108.4	乙酰基 CO		170.3			
4	182.6	182.5	182.5	182.6	182.7	乙酰基 CH_3		21.0			
4a	104.5	104.5	104.3	104.7	104.4	当归酰基 α-CH_3			20.5	20.5	
5	159.8	159.6	159.5	159.2	160.0	当归酰基 β-CH_3			15.7	15.7	
6	103.1	102.5	102.6	102.9	104.1	当归酰基 C═			127.6	127.4	
7	159.1	158.8	158.9	159.5	159.6	当归酰基 ═C			138.9	139.0	
8	94.9	94.8	94.7	94.9	94.9	当归酰基 C═O			166.9	167.0	
8a	156.3	156.3	156.2	155.9	156.3	葡萄糖 1′					102.4
2-CH_2R^1	20.6	20.5	20.5	61.3	20.1	葡萄糖 2′					74.9
2′	78.6	76.8	76.9	76.7	78.4	葡萄糖 3′					78.4
3′	68.9	69.8	69.7	69.5	74.3	葡萄糖 4′					71.8
4′	25.5	22.6	22.7	22.7	22.3	葡萄糖 5′					78.4
CH_3	22.1	23.0	22.9	22.9	22.3	葡萄糖 6′					63.0

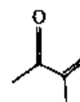
① 化合物 29 在 C_5D_5N 中测定。



25. R^1 = H，R^2 = H

26. R^1 = H，R^2 = CH_3CO

27. R^1 = H，R^2 = 

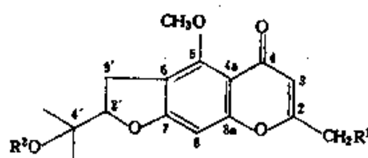
28. R^1 = OH，R^2 = 

29. R^1 = H，R^2 = Glu

表 22-32　色原酮类化合物 30～34 的 ^{13}C-NMR 化学位移数据[60]①

C \ 化合物	30	31	32	33	34	C \ 化合物	30	31	32	33	34
2	163.4	163.5	167.3	162.7	160.8	CH_3	26.2	23.5	26.2	26.0	25.6
3	111.6	111.5	109.3	110.9	111.2	OCH_3	60.9	60.8	60.9	60.8	61.0
4	176.5	176.7	176.9	176.6	176.6	葡萄糖 1′		98.9		104.0	99.9
4a	112.2	112.2	112.7	112.5	112.4	葡萄糖 2′		75.0		74.8	71.1
5	165.2	164.9	165.3	165.3	164.7	葡萄糖 3′		78.5		78.4	72.7
6	118.2	118.0	118.3	118.1	117.4	葡萄糖 4′		71.5		71.4	68.2
7	160.1	159.9	159.9	159.7	159.5	葡萄糖 5′		77.8		78.1	72.1
8	93.9	93.9	94.0	94.0	93.8	葡萄糖 6′		62.5		62.6	61.8
8a	156.2	156.2	156.3	156.1	156.1	乙酰基 CH_3					20.6(2C)
2-CH_2R^1	19.3	19.4	60.8	66.4	66.3						20.7(2C)
2′	92.2	91.0	92.2	92.1	91.4	乙酰基 CO					169.3(2C)
3′	27.9	28.2	28.0	27.9	27.8						170.2
4′	70.8	77.8	70.8	70.8	71.6						170.6
CH_3	25.6	22.5	25.7	25.6	24.4						

① 化合物 30～33 在 C_5D_5N 中测定。



30. $R^1 = R^2 = H$
31. $R^1 = H$, $R^2 = GLu$
32. $R^1 = OH$, $R^2 = H$
33. $R^1 = -O$-Glu, $R^2 = H$
34. $R^2 = -O$-Glu Ac_4, $R^2 = H$

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第二十三章　香豆精和蒽醌类化合物的^{13}C-NMR化学位移

香豆精化合物的^{13}C-NMR化学位移特征：

① 简单香豆精的^{13}C-NMR谱中，母核C-2羰基处于最低场，一般在$\delta=159\sim162$。C-9的化学位移，由于受α-吡喃环的氧的影响，一般情况下在$\delta=149\sim154$。C-6或C-8有羟基时，C-9向高场位移7～11个δ单位左右，而7-甲基、7-羟基、7-甲氧基使C-9向低场位移0.8～2.3个δ单位。C-3有羟基或甲氧基取代时，C-3向低场位移26左右，C-4向高场位移29左右。C-4位有羟基或甲氧基取代时，C-4向低场位移22左右，C-3向高场位移24～26左右。如果在芳环中有羟基取代时，α碳向低场位移29～30左右，β碳向高场位移11～16左右，对γ碳的影响较小。在芳环中有甲基时，α碳向低场位移5～12左右，对β、γ碳影响较小。酚羟基和糖成甙时，α碳向高场位移0.6～1.3左右，β碳向低场位移0.5～1.5左右。

② 呋喃香豆精和吡喃香豆精中，由于呋喃环和吡喃环是通过7位的氧与母核相并合，所以C-7的化学位移在$\delta=155\sim162$之间。

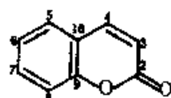
③ 3-苯基异香豆精C-4的化学位移为$\delta=99.0\sim101.7$，C-3为$\delta=150.6\sim153.4$，羰基为$\delta=162.0\sim162.6$；4-苯基异香豆精C-4的化学位移为$\delta=117.0\sim118.7$，C-3为$\delta=140.3\sim143.3$，羟基为$\delta=160.2\sim161.9$。

第一节　香豆精及异香豆精类化合物的^{13}C-NMR化学位移

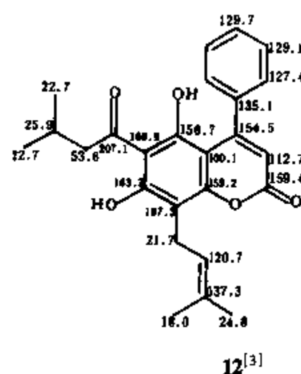
一、香豆精类化合物的^{13}C-NMR化学位移

表23-1　香豆精类化合物1～11的^{13}C-NMR化学位移数据[1,2]

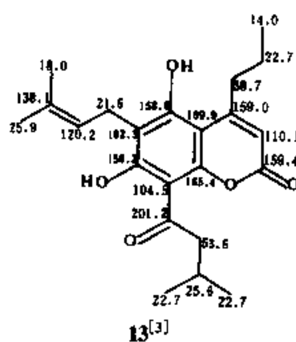
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
2	159.8	158.5	162.2	161.6	159.4	160.1	160.7	160.0	159.9	160.8	159.9
3	115.8	141.75	91.4	125.5	114.0	116.1	111.5	116.1	115.5	115.3	
4	142.8	115.0	165.8	138.8	151.4	143.8	144.3	144.5	142.6	143.1	143.1
5	127.4	126.3	123.3	126.7	123.9	112.4	129.55	118.4	127.0	127.4	125.0
6	123.8	124.5	123.7	123.9	123.4	153.7	113.3	124.4	133.2	125.4	123.3
7	131.1	127.5	132.4	130.1	130.8	119.7	161.6	118.4	131.9	142.9	132.4
8	115.8	115.6	116.3	116.0	115.8	116.9	102.5	144.7	115.5	116.8	125.2
9	153.3	149.2	153.8	153.0	152.6	146.75	155.7	142.4	151.3	154.3	151.6
10	118.2	120.7	116.1	119.3	119.0	119.1	111.5	119.7	117.7	116.3	117.8
CH_3				16.7	17.5				19.8	21.4	14.4



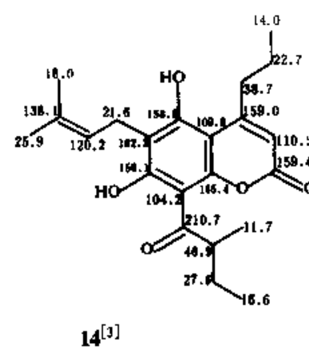
1. —　**2.** 3-OH　**3.** 4-OH　**4.** 3-CH_3　**5.** 4-CH_3　**6.** 6-OH　**7.** 7-OH　**8.** 8-OH　**9.** 6-CH_3　**10.** 7-CH_3　**11.** 8-CH_3



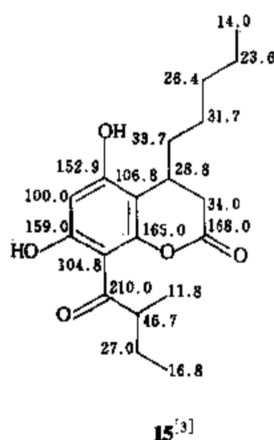
12[3]



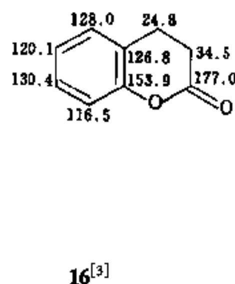
13[3]



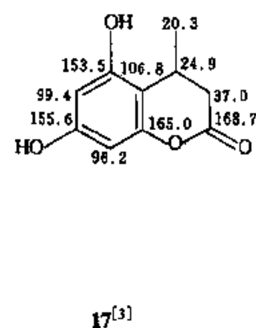
14[3]



15[3]



16[3]

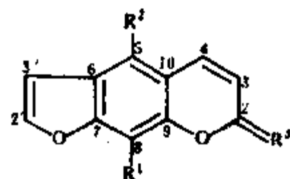


17[3]

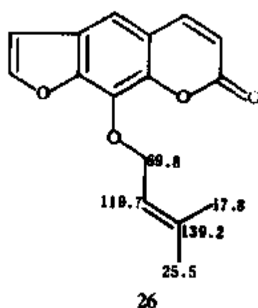
表 23-2 呋喃香豆精化合物 18～30 的^{13}C-NMR 化学位移数据[4,5]①

C \ 化合物	18	19	20	21	22	23	24	25	26	27	28	29	30
2	161.1	160.0	160.4	160.3	197.2	160.5	159.7	159.7	160.2	161.6	161.1	161.5	160.5
3	114.7	113.7	114.5	112.8	125.3	112.8	112.2	112.6	114.2	112.9	114.1	110.5	111.2
4	144.2	145.3	144.4	139.4	131.2	139.5	139.6	139.1	144.3	155.7	144.2	139.2	144.6
5	120.0	110.1	113.1	149.6	149.4	144.4	141.0	146.7	113.2	112.3	118.8	152.7	123.8
6	125.0	125.2	126.2	113.0	113.1	114.9	114.7	113.6	125.7	125.6	126.5	105.9	125.5
7	156.6	145.3	147.6	158.5	157.9	149.9	146.9	149.9	148.3	153.4	156.3	165.5	163.3
8	99.9	130.1	132.7	94.0	92.7	128.3	125.3	118.1	131.2	116.2	99.1	92.9	96.7
9	152.2	139.8	142.9	152.7	154.2	143.7	139.6	143.8	143.5	149.1	151.5	156.6	155.1
10	115.6	116.2	116.5	106.7	107.4	107.7	107.1	106.9	116.2	109.3	115.0	110.4	121.1
2'	147.0	147.2	146.6	145.0	146.4	145.3	146.0	145.1	146.4	157.6	167.3	72.4	91.0
3'	106.6	106.9	106.8	105.3	105.6	105.3	105.1	105.3	106.6	102.9	99.5	28.3	28.7
OCH_3			61.2	60.3	60.1	61.9 61.7	60.9	60.3				59.4	

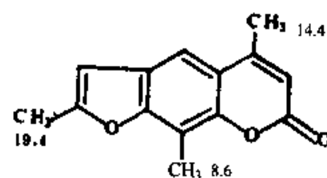
① 全部化合物在重氢二甲基亚砜中测定。



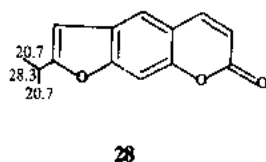
18. $R^1 = R^2 = H$, $R^3 = O$
19. $R^1 = OH$, $R^2 = H$, $R^3 = O$
20. $R^1 = OCH_3$, $R^2 = H$, $R^3 = O$
21. $R^1 = H$, $R^2 = OCH_3$, $R^3 = H$
22. $R^1 = H$, $R^2 = OCH_3$, $R^3 = S$
23. $R^1 = R^2 = OCH_3$, $R^3 = O$
24. $R^1 = OCH_3$, $R^2 = OH$, $R^3 = O$
25. $R^1 = OCH_3$, $R^2 = OAc$, $R^3 = O$



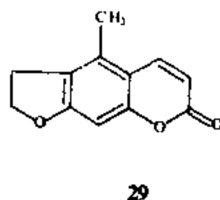
26



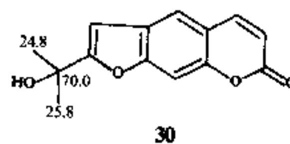
27



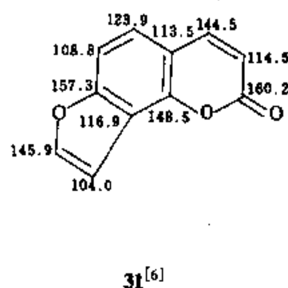
28



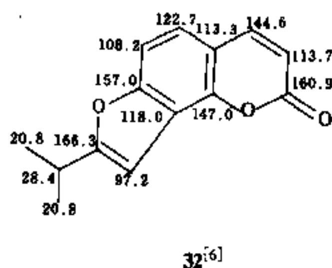
29



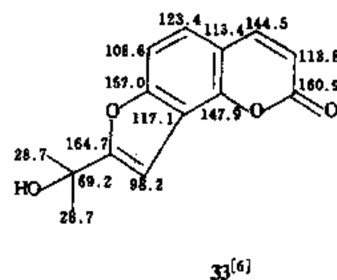
30



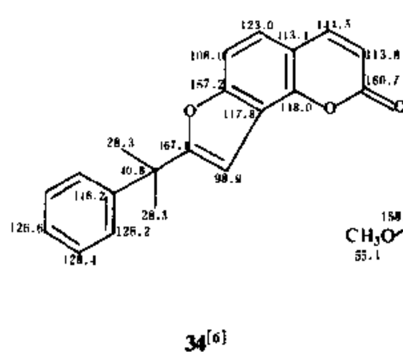
31[6]



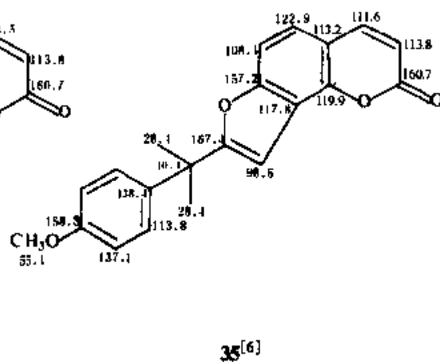
32[6]



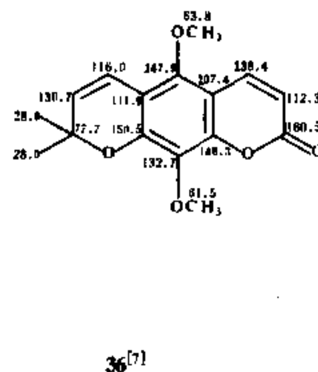
33[6]



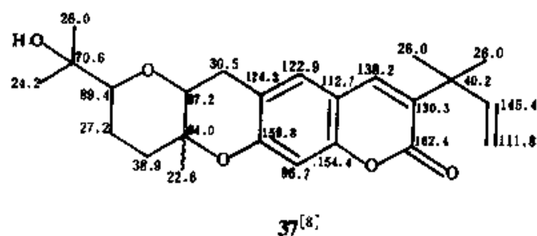
34[6]



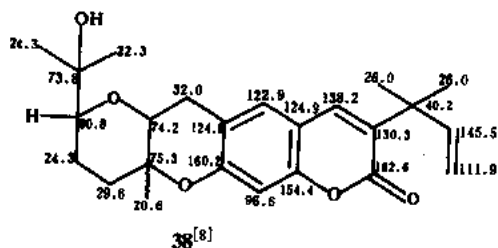
35[6]



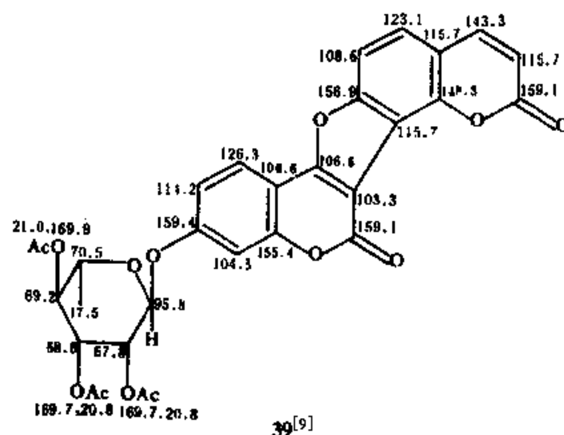
36[7]



37[8]



38[8]

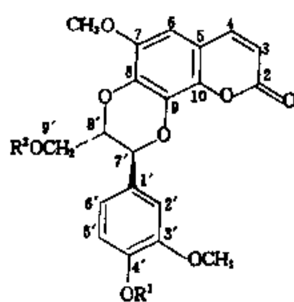


39[9]

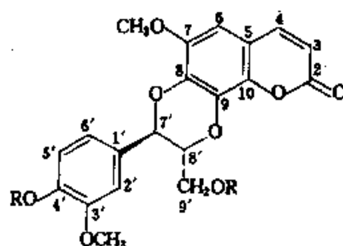
表 23-3 香豆精木脂素类化合物 40～45 的 ^{13}C-NMR 化学位移数据[10,11,12]

C \ 化合物	40	41	42	43	44	45
2	160.8	160.7	160.4	160.7	160.4	160.2
3	113.6	113.3	114.4	113.8	114.3	114.1
4	144.5	144.5	143.5	144.4	143.5	143.5
5	101.1	101.0	100.5	101.2	100.8	101.1
6	146.3	146.3	145.8	146.2	145.7	145.8
7	138.4	138.2	136.9	138.1	136.3	136.9
8	133.0	132.0	133.5	133.2	132.1	131.6
9	139.3	139.2	140.8	139.4	140.7	145.7
10	111.9	112.2	111.9	111.8	111.8	111.8
1′	127.5	129.1	131.7	127.5	133.5	133.1
2′	112.3	111.6	111.5	112.3	111.3	104.5
3′	150.0	150.1	151.7	150.1	151.6	152.7
4′	149.0	149.6	138.8	149.1	138.8	138.7

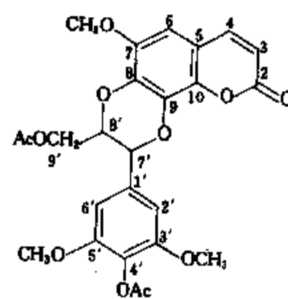
C \ 化合物	40	41	42	43	44	45
5′	116.6	113.8	123.3	116.5	123.2	152.7
6′	121.7	121.0	119.9	121.7	119.8	104.5
7′	75.5	77.3	76.7	77.1	76.0	77.0
8′	79.9	79.7	75.1	80.2	75.6	75.0
9′	60.7	60.6	62.4	61.1	62.4	62.3
OCH_3	55.8	55.7	56.0	55.9	56.0	56.2
	65.2	56.1	56.1	56.1	56.4	
		64.4				
		14.9				
$CCOCH_3$			168.5		168.6	168.2
			170.2		170.2	21.0
			20.6		20.6	170.1
						21.2



40. $R^1 = R^2 = H$
41. $R^1 = C_2H_5$, $R^2 = H$
42. $R^1 = R^2 = COCH_3$



43. R = H
44. R = $COCH_3$

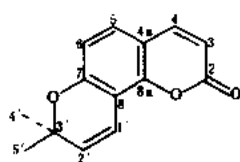


45

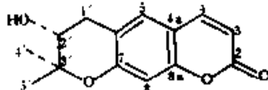
表 23-4a　香豆精类化合物 46～58 的^{13}C-NMR 化学位移和 C—H 偶合常数数据[13]

C ＼ 化合物	46	47	47①	48	49	50	51	52	53	54①	55	56①	57	58
2	162.9	160.9	160.0	160.5	160.3	160.4	161.0	154.2	160.3	159.4	160.3	160.4	160.7	160.7
3	111.2	112.4	112.5	112.3	112.8	112.2	111.5	118.4	111.8	112.9	112.3	111.8	111.5	112.5
	(172.8)			(172.8)		(171.9)	(171.6)		(173.0)	(172.5)	(173.0)	(172.8)		
4	144.6	143.5	143.6	144.2	143.4	143.5	143.6	138.7	144.8	143.0	138.5	139.9	144.3	143.0
	(161.6,			(168.2)		(162.8,	(161.8,		(165.3,	(165.3,	(166.6)	(170.6)		
	5.33					5.4)	5.2)		5.2)	5.4)				
4a	111.8	112.6	117.6	112.3	114.3	112.2	111.2	111.1	111.9	112.3	106.6	106.4	111.5	112.1
5	127.8	126.0	126.0	129.4	120.8	127.5	125.9	125.0	129.0	129.1	147.8	149.1	129.5	128.3
	(158.0)			(162.4)		(163.5,	(162.8,		(165.7,	(163.1				
						3.9)	4.0)		4.7)	4.0)				
6	126.4	107.1	107.1	118.1	118.9	114.6	114.1	119.3	114.1	114.1	113.5	113.2	113.3	112.7
						(165.5)	(163.9)		(164.7)					
7	158.9	159.9	159.9f	156.6	148.9	155.9	157.2	152.4	156.2	156.7	157.4	157.6	161.6	161.7
8	102.7	117.4	112.5	103.2	135.1	108.8	108.8	110.5	109.0	107.2	93.8	93.0	102.5	101.3
	(164.8)			(164.6)							(169.6)	(169.3)		
8a	153.8	152.4	152.5	153.6	147.9	149.8	152.8	149.7	150.8	153.8	151.9	152.1	155.7	155.4
1′	27.5	21.6	21.6	30.4	118.9	113.1	16.1	16.8	59.9	68.6				65.2
	(127.4)			(126.6)		(164.9)	(132.5)		(154.3)	(147.4)				
2′	121.0	120.9	120.8	67.6	130.9	130.4	31.1	31.0	70.1	73.7	144.8	145.4		118.2
	(155.8)			(151.4)		(161.3)	(125.6)		(154.0)	(152.1)	(205.1,	(205.7		
											9.9)	9.7)		
3′	137.5	132.1	132.2	78.7	77.5	77.2	75.1	76.5	77.1	78.5	104.1	105.5		141.2
											(178.8,	(180.7,		
											13.2)	14.0)		
4′	15.9	17.5	17.7	21.2	27.9	27.8	26.2	26.3	22.1	23.5				16.5
	(125.8)			(126.4)		(128.5)	(126.7)		(126.1)	(125.5)				
5′	39.4	25.4	25.5	25.6	27.9	27.8	26.2	26.3	25.2	24.3				39.2
	(126.0)			(125.0)		(128.5)	(126.7)		(125.2)	(126.8)				
6′,1″	26.4								166.2		71.8	74.7		26.0
1‴	(126.8)								165.9		(145.2)	(144.7)		
7′,2″	123.7								127.2		60.7	76.6		123.3
2‴	(160.7)								126.8		(166.5)	(143.6)		
8′,3″	131.2								139.3		57.8	70.9		131.4
3‴									(165.0)					
									137.8					
									(162.5)					
9′,4″	17.4								15.2		18.5	24.7		17.5
4‴	(126.5)								(128.4)		(126.5)	(127.8)		
									15.4					
									(130.2)					
10′,5‴	25.4								20.0		24.1	27.4		25.4
5‴	(126.1)								(128.8)		(127.3)	(128.8)		
OCH_3					60.9					57.8				
										(141.6)				
$OCOCH_3$														

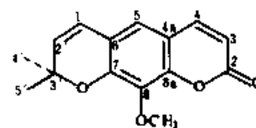
① 化合物 47,54,56 在$(CD_3)_2SO$中测定。



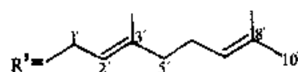
46. $R^1 = R^2 = H$,



48



49

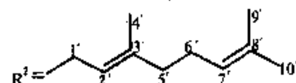


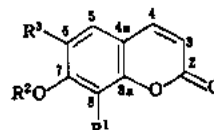
47. R^1= (prenyl),

$R^2 = CH_3$, $R^3 = H$

57. $R^1 = R^2 = R^3 = H$

58. $R^1 = R^3 = H$,

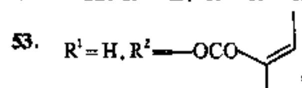




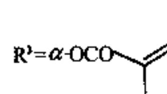
51. $R^1 = R^2 = R^3 = H$

52. $R^1 = Cl$, $R^2 = R^3 = H$

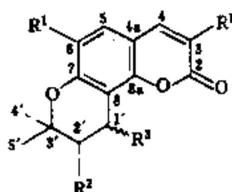
53. $R^1 = H$, R^2=



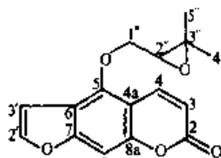
$R^3 = \alpha$-OCO



54. $R^1 = H$, $R^2 = OH$, $R^3 = \beta$-OCH_3



50



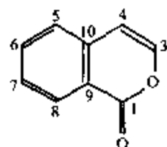
55

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二、异香豆精类化合物的¹³C-NMR 化学位移

表 23-4b　异香豆精化合物 59～62 的¹³C-NMR 化学位移数据[13a]

化合物 / C	59	60	61	62	化合物 / C	59	60	61	62
1	162.0	162.6	161.9	160.2	CO				168.6
3	153.2	150.6	140.3	143.3					168.3
4	101.7	100.0	118.7	117.0	$COCH_3$				20.9
5	127.9	127.5	156.6	146.2					19.3
6	134.6	134.7	106.3	120.6	1′	131.8	113.7	136.7	134.8
7	129.4	129.1	160.3	150.0	2′	125.1	162.0	127.1	128.1
8	125.8	126.2	102.4	124.0	3′	128.7	105.4	129.1	129.8
9	120.4	120.2	123.3	123.4	4′	129.8	158.6	126.9	127.8
10	137.3	138.4	120.2	126.7	5′	128.7	105.1	129.1	129.8
OCH_3		55.6	55.4		6′	125.1	129.6	127.1	128.1
		55.4	55.7						



59. 3-苯基
60. 3-（2′，4′-二甲氧基苯基）
61. 5，7-二甲氧基-4-苯基
62. 5，7-二乙酰基-4-苯基

第二节　蒽醌类化合物的^{13}C-NMR化学位移

表 23-5　蒽醌类化合物 1～8 的^{13}C-NMR 化学位移数据[14]①

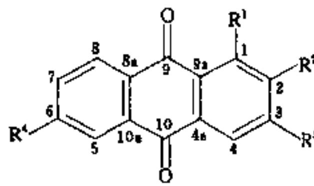
C \ 化合物	1	2	3	4	5	6	7	8
1	150.66	163.63	162.01	163.63	163.57	161.78	150.95	163.4
2	152.56	117.05	117.10	120.56	120.56	123.50	151.53	120.1
3	120.91	164.03	162.71	159.94	160.17	161.67	120.68	163.0
4	120.62	107.65	106.78	105.22	105.05	106.21	120.21	107.7
4a	123.50	133.59	131.46	135.21	135.27	133.54	125.69	133.9
5	126.44	126.62	112.20	112.60	112.72	126.73	126.56	126.5
6	134.74	134.46	161.67	161.27	161.32	134.51	134.98	134.3
7	133.65	134.28	120.85	121.48	121.43	134.51	134.11	133.1
8	126.16	126.21	128.98	129.56	129.62	126.33	126.39	126.2
8a	133.31	132.67	124.54	124.31	124.43	132.55	133.13	131.7
9	188.43	185.89	185.25	186.18	186.23	186.81	188.20	185.9
9a	115.89	108.86	108.34	110.59	110.58	111.22	116.11	110.6
10	180.06	181.44	181.56	181.56	181.56	181.21	180.64	181.5
10a	132.50	132.84	131.46	131.86	131.92	132.67	132.73	132.7
2-CH_3			7.90	8.76	8.76			
2-$CH_2OC_2H_5$		65.21						
		59.21						
		15.28						
2-CH_2OH						50.19		51.2

① 在 $(CD_3)_2SO$ 中测定。

表 23-6　蒽醌类化合物 4～7 中糖部分的^{13}C-NMR 化学位移数据[14]①

C \ 化合物	4	5	6	7	C \ 化合物	4	5	6	7
	Glu	Glu	Glu	Glu	Ac-CO	170.26			
1′	97.44	97.50	100.67	99.69		Rham	Rham	Xyl	Xyl
2′	76.45	76.46	73.11	72.88	1″	100.27	100.21	103.90	103.84
3′	77.09	77.09	75.65	75.93	2″	70.46	70.46	73.11	73.28
4′	70.11	69.59	69.07	69.42	3″	70.46	70.46	76.22	76.28
5′	74.09	77.38	75.65	75.93	4″	72.01	72.01	69.36	69.42
6′	63.37	60.31	67.86	68.15	5″	68.56	68.50	68.50	65.44
Ac-CH_3	20.41				6″	18.10	18.10		

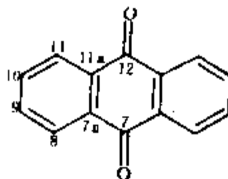
① 在 $(CD_3)_2SO$ 中测定。



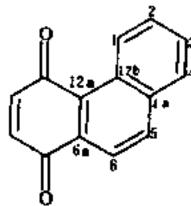
1. $R^1 = R^2 = OH$, $R^3 = R^4 = H$
2. $R^1 = R^3 = OH$, $R^2 = CH_2OCH_2CH_3$, $R^4 = H$
3. $R^1 = R^3 = R^4 = OH$, $R^2 = CH_3$
4. $R^1 = R^4 = OH$, $R^2 = CH_3$, $R^3 = O$-（O-6′-Ac） glu$\underline{21}$rham
5. $R^1 = R^4 = OH$, $R^2 = CH_2OH$, $R^3 = O$-glu$\underline{21}$rham
6. $R^1 = OH$, $R^2 = CH_2OH$, $R^3 = O$-glu$\underline{61}$xyl, $R^4 = H$
7. $R^1 = OH$, $R^2 = O$-glu$\underline{61}$xyl, $R^3 = R^4 = H$
8. $R^1 = R^3 = OH$, $R^2 = CH_2OH$, $R^4 = H$

表 23-7　蒽醌类化合物 9 ~ 19 的^{13}C-NMR 化学位移数据[15]

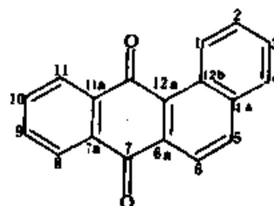
C \ 化合物	9	10	11	12	13	14	15	16	17	18	19
1	—	127.7	128.4	156.2	106.2	130.2	120.3	128.3	128.7	128.3	128.7
2	—	130.0	129.6	109.0	161.1	122.2	130.0	129.6	192.5	129.7	129.0
3	—	128.5	128.4	129.7	121.5	159.3	106.4	128.3	128.5	128.3	128.4
4	—	128.5	128.4	120.5	129.9	106.6	155.1	128.5	128.5	128.6	128.6
5	—	134.9	134.9	132.9	134.9	133.5	129.1	135.0	134.6	135.1	133.8
6	—	121.7	122.2	122.2	120.4	123.1	121.5	122.6	122.3	122.4	121.6
8	127.0	—	126.1	126.0	126.2	126.2	126.2	159.4	108.9	128.8	118.9
9	133.9	—	133.1	132.5	133.1	133.2	133.1	116.9	163.5	120.3	134.0
10	133.9	—	133.8	133.8	133.9	133.8	133.9	134.9	121.1	164.2	117.8
11	127.0	—	126.9	126.3	126.9	127.0	127.0	119.6	129.5	110.0	159.2
7	182.8	185.6	183.5	182.5	183.8	186.0	183.8	182.9	183.7	182.4	184.0
12	182.8	187.9	185.7	185.7	185.9	183.5	185.8	186.0	185.0	185.7	185.9
4a	—	136.2	136.3	137.9	132.3	138.6	128.8	135.9	136.6	136.2	136.6
6a	133.3	131.8	133.7	133.3	134.3	132.1	134.1	135.5	133.9	134.0	132.0
7a	133.3	—	131.9	132.2	132.1	131.8	132.1	120.4	133.8	125.5	134.4
11a	133.3	—	134.7	136.8	134.9	134.8	135.0	137.2	128.4	136.8	123.8
12a	133.3	126.8	129.0	136.3	127.2	129.2	128.0	—	129.1	128.1	132.3
12b	—	129.6	130.2	121.1	132.1	125.5	131.4	129.8	130.4	130.3	129.7
OCH_3	—	—	—	56.0	55.5	55.3	55.3	56.5	55.8	55.8	56.6



9



10

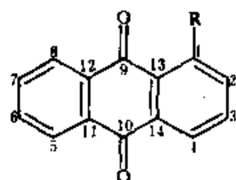


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12. 1-OCH_3
13. 2-OCH_3
14. 3-OCH_3
15. 4-OCH_3
16. 8-OCH_3
17. 9-OCH_3
18. 10-OCH_3
19. 11-OCH_3

表 23-8　1-取代的蒽醌 20 ~ 30 的 ^{13}C-NMR 化学位移数据[16]

C＼化合物	20	21	22	23	24	25	26	27	28	29	30
1	127.2	161.5	134.8	122.4	92.8	141.9	160.3	150.2	162.4	150.8	141.9
2	134.1	122.6	137.4	141.2	148.2	138.0	117.9	129.9	124.1	123.4	125.9
3	134.1	134.9	134.2	134.3	134.0	132.9	134.9	134.3	136.5	134.2	135.6
4	127.2	123.1	126.4	127.5	128.2	125.9	119.8	125.7	119.3	116.6	122.3
5	127.2	126.8	126.4	126.7	126.3	126.5	126.5	126.9	127.2	126.1	127.1
6	134.1	133.5	133.3	133.5	133.4	133.3	133.1	133.9	134.4	132.5	134.1
7	134.1	134.0	133.5	133.7	133.5	133.9	134.2	134.3	133.9	133.2	134.1
8	127.2	126.6	127.2	127.3	127.3	127.0	127.2	127.2	126.7	126.1	127.1
9	183.1	180.5	181.2	181.2	180.8	184.8	182.4	181.7	188.4	184.5	187.0
10	183.1	181.6	181.7	181.4	181.2	183.3	183.3	182.4	182.1	182.8	182.3
11	133.5	132.3	132.1	132.5	132.2	132.7	132.5	132.6	133.5	132.7	133.7
12	133.5	133.8	134.2	134.0	134.0	134.6	135.7	134.1	133.5	132.7	133.7
13	133.5	121.0	129.3	132.5	135.4	134.8	121.6	124.9	116.0	113.2	117.4
14	133.5	135.0	135.8	134.4	132.0	131.0	134.9	135.3	133.1	134.0	132.7
其他碳						23.3	56.5	21.1			25.7
								169.5			169.7

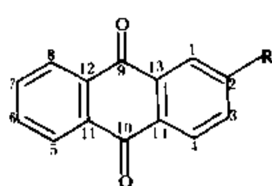


20. R = H
21. R = F
22. R = Cl
23. R = Br
24. R = I
25. R = CH_3
26. R = OCH_3
27. R = $OCOCH_3$
28. R = OH
29. R = NH_2
30. R = $NHCOCH_2$

表 23-9　2-取代蒽醌 31 ~ 43 的 ^{13}C-NMR 化学位移数据[17]①

C＼化合物	31	32	33	34	35	36	37	38	39	40	41	42	43
1	127.2	113.5	126.7	128.3	135.7	126.5	131.4	110.1	121.9	120.0	112.2	109.3	115.6
2	134.1	166.3	140.5	128.5	101.7	144.3	117.6	164.4	147.7	155.3	163.1	153.9	144.6
3	134.1	121.3	134.3	136.4	142.5	132.8	136.5	121.1	129.9	127.4	121.5	117.9	123.4
4	127.2	130.5	128.4	128.2	128.0	126.5	127.9	129.7	127.0	129.3	129.7	128.7	128.1
5	127.2	127.4	126.7	126.4	126.7	126.3	127.5	127.1	126.7	127.2	126.5	125.7	126.3
6	134.1	134.0	133.8	133.1	133.8	133.1	134.7	133.5	133.3	134.3	134.3	133.3	134.0
7	134.1	134.1	134.0	133.2	133.8	134.0	134.7	134.0	133.4	134.1	133.8	132.5	133.9
8	127.2	127.2	126.7	126.4	126.7	126.3	127.5	127.1	126.7	127.2	126.5	125.7	126.3
9	183.1	181.5	181.3	181.1	181.2	181.8	181.6	183.1	182.4	181.9	182.5	182.6	182.1
10	183.1	181.2	181.3	181.0	181.8	182.2	180.9	181.8	181.8	182.1	181.0	179.5	181.0
11	133.5	133.2	132.7	132.5	132.5	132.8	133.0	133.8	133.7	133.4	133.0	133.3	133.0
12	133.5	133.2	132.7	132.5	132.7	132.8	133.1	133.7	133.7	133.1	133.1	132.6	133.0
13	133.5	135.8	134.1	134.0	133.4	132.7	133.8	135.7	133.5	135.1	135.1	134.4	134.2
14	133.5	129.7	131.1	131.2	131.9	130.6	135.6	127.3	129.4	131.0	125.1	121.2	127.6
其他碳						21.0	117.0	55.8	14.6	21.0			23.9
										168.5			168.9

① 在 $(CD_3)_2SO$ 中测定。



31. R = H
32. R = F
33. R = Cl
34. R = Br
35. R = I
36. R = CH_3
37. R = CN
38. R = OCH_3
39. R = SCH_3
40. R = $OCOCH_3$
41. R = OH
42. R = NH_2
43. R = $NHCOCH_3$

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第二十四章　木脂素类化合物的^{13}C-NMR 化学位移

木脂素类化合物是一类由双分子或三分子苯丙素衍生物聚合而成的化合物，有很多类型。它们的^{13}C-NMR 化学位移的特征如下：

① 苯环上多联有 OCH_3，其化学位移一般为 $\delta = 55 \sim 62$，有时联有 OCH_2O，它的化学位移一般为 $\delta = 100 \sim 102$。

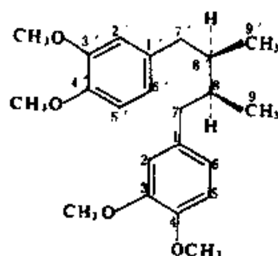
② 苯环上的各碳的化学位移基本与取代的苯环的化学位移相同。

③ 除两个苯环以外的六个碳可以为侧链，也可以为形成不同的环系，解析这些碳的化学位移对形成环系的构型是非常有意义的。例如，联苯类木脂素中形成环辛烯环中，C-9′为 a 键甲基，化学位移在高场，一般为 $\delta = 12.3 \sim 12.4$；C-9 为 e 键甲基，化学位移一般在低场，为 $\delta = 21.8 \sim 21.9$；C-9′为 e 键甲基，化学位移在低场；C-9 为 a 键甲基，化学位移在高场。

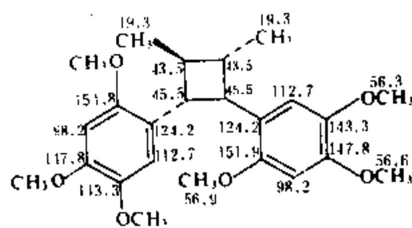
第一节　丁烷衍生物类木脂素的^{13}C-NMR 化学位移

表 24-1　丁烷衍生物类木脂素 1～11 的^{13}C-NMR 化学位移数据[1～4]

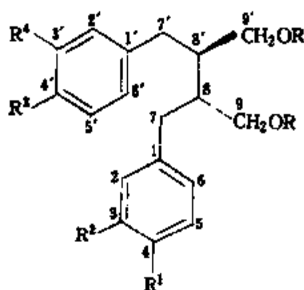
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
1	134.5	132.4	137.9	132.2	138.5	132.9	131.9	133.7	134.3	135.2	133.2
2	112.4	111.7	112.7	111.4	112.8	110.0	110.0	111.2	107.9	108.2	108.0
3	148.8	146.6	150.8	146.3	150.8	148.7	148.7	148.8	147.3	147.8	147.5
4	147.2	143.7	138.4	143.6	138.0	147.0	147.2	147.2	145.5	145.9	145.7
5	111.2	114.3	120.8	114.0	122.8	112.0	111.8	112.4	109.2	109.6	109.0
6	121.0	121.5	122.4	121.4	120.9	120.8	120.7	121.2	121.7	122.2	121.7
7	38.9	35.8	35.2	35.8	35.4	35.7	34.8	35.0	35.7	34.9	34.8
8	39.2	43.7	39.5	43.8	39.7	43.8	39.6	40.8	44.1	41.4	39.9
9	16.3	60.5	64.1	60.4	64.2	60.3	64.2	72.7	59.8	72.7	64.2
1′	134.5	132.4	137.9	133.0	138.5	132.9	131.9	133.7	134.3	135.2	133.2
2′	112.4	111.7	112.7	111.0	112.8	110.0	111.0	111.2	107.9	108.2	108.0
3′	148.8	146.6	150.8	148.6	150.8	148.7	148.7	148.8	147.3	147.8	147.5
4′	147.2	143.7	138.4	147.0	138.0	147.0	147.2	147.2	145.5	145.9	145.7
5′	111.2	114.3	120.8	112.0	122.4	112.0	111.8	112.8	109.2	109.6	109.0
6′	121.0	121.5	122.4	120.8	120.9	120.8	120.7	121.2	121.7	122.2	121.7
7′	38.9	35.8	35.2	35.8	35.4	35.7	34.8	35.0	35.7	34.9	34.8
8′	39.2	43.7	39.5	43.8	39.7	43.8	39.6	40.8	44.1	41.4	39.9
9′	16.3	60.5	64.1	60.4	64.2	60.3	64.2	72.7	59.8	72.7	64.2
OCH_3	55.8	55.7	55.7	55.7	55.7	55.7	55.7	55.7		58.8	
	55.9				55.8			55.9			
—OCH_2O								58.7			
$OCOCH_3$									100.6	100.9	100.7
			170.7		170.7		170.6				170.8
			20.8		21.0		20.9				20.9
			168.8		168.8						
			20.6		20.7						



1

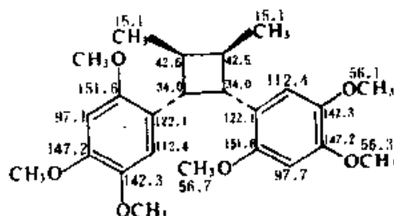


12[5]



2~11

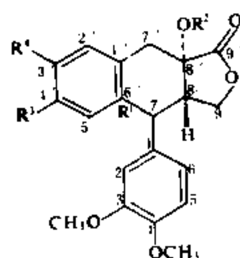
取代基 / 化合物	R	R¹	R²	R³	R⁴
2	H	OH	OCH_3	OCH_3	OH
3	Ac	OAc	OCH_3	OCH_3	OAc
4	H	OH	OCH_3	OCH_3	OCH_3
5	Ac	OAc	OCH_3	OCH_3	OCH_3
6	H	OCH_3	OCH_3	OCH_3	OCH_3
7	Ac	OCH_3	OCH_3	OCH_3	OCH_3
8	CH_3	OCH_3	OCH_3	OCH_3	OCH_3
9	H	OCH_2O		OCH_2O	
10	CH_3	OCH_2O		OCH_2O	
11	Ac	OCH_2O		OCH_2O	



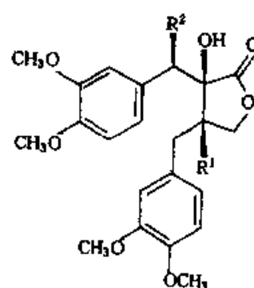
13[6]

表 24-2 丁烷衍生物类木脂素 14~23 的^{13}C-NMR 化学位移数据[7~9]

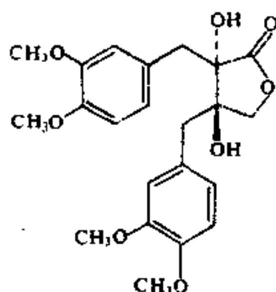
化合物 / C	14	15	16	17	18	19	20	21	22	23
1	131.1	130.3	133.9	130.4	130.1	125.5	132.9	125.7	126.1	127.1
2	111.6	111.6	109.0	109.9	110.7	111.2	111.3	108.4	108.5	108.4
3	146.6	148.0	145.2	149.2	147.8	148.9	148.1	149.2	148.4	148.0
4	149.2	149.2	148.6	151.2	149.2	149.1	150.2	146.6	146.6	146.6
5	112.8	111.8	112.9	114.5	111.4	111.4	113.6	111.4	108.8	109.0
6	120.9	120.5	117.6	122.8	120.6	122.2	122.3	121.9	122.1	121.9
7	31.6	33.5	70.0	73.1	31.8	39.1	37.6	37.5	37.6	37.8
8	43.8	42.7	48.1	45.5	47.5	78.1	77.0	39.6	39.9	39.4
9	70.2	71.8	79.2	67.8	70.1	74.1	74.2	69.5	69.5	69.7
1′	126.2	132.7	126.2	131.9	130.9	126.6	135.4	126.9	128.2	129.4
2′	112.3	111.6	111.4	111.2	110.7	111.2	111.7	109.1	108.7	107.4
3′	145.1	151.2	146.8	151.2	148.7	149.1	149.3	150.8	149.2	153.4
4′	147.9	139.5	149.2	139.5	149.6	148.9	150.6	148.0	148.0	157.4
5′	114.4	114.9	114.4	119.1	111.7	113.4	114.7	113.0	109.2	153.4
6′	123.2	122.9	123.2	122.8	111.9	122.5	123.3	123.0	125.9	107.4
7′	42.0	43.2	42.9	41.5	76.9	37.8	37.1	137.4	137.2	137.6
8′	76.5	80.2	79.2	80.4	75.4	78.6	79.0	131.5	131.5	131.3
9′	178.6	174.9	178.7	174.0	177.8		181.3	172.5	172.5	172.3
OCH_3	55.9	55.9	56.1	55.9	55.9	55.9	56.8 55.9	56.0		56.3 60.9
OCH_2O								101.1	101.8 104.0	101.1
$OCOCH_3$		168.9 20.5 170.3 20.5		168.9 20.7 169.3 20.7 170.3 20.9						



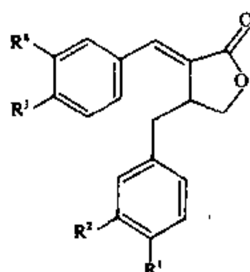
14. $R^1 = R^2 = H$, $R^3 = OH$, $R^4 = OCH_3$
15. $R^1 = H$, $R^2 = R^3 = OAc$, $R^4 = OCH_3$
16. $R^1 = R^2 = R^3 = OH$, $R^4 = OCH_3$
17. $R^1 = R^3 = OAc$, $R^2 = Ac$, $R^4 = OCH_3$



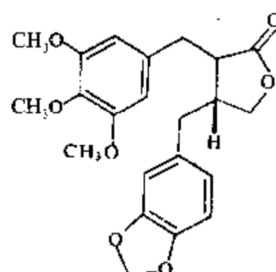
18. $R^1 = H$, $R^2 = OH$
19. $R^1 = OH$, $R^2 = H$



20



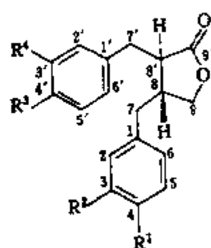
21. $R^1 = R^2 = R^3 = R^4 = OCH_3$
22. $R^1 + R^2 = OCH_2O$, $R^3 + R^4 = OCH_2O$

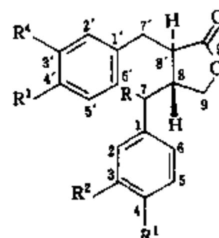


23

表 24-3　丁烷衍生物类木脂素 24～37 的 ^{13}C-NMR 化学位移数据[10～13]

化合物 / C	24	25	26	27	28	29	30	31	32	33	34	35	36	37
1	129.6	136.8		131.1	131.1	131.0	130.9	129.5	133.6	136.1	134.1	129.6	135.3	130.7
2	111.0	112.7	116.3	109.2	109.3	109.0	112.9	111.2	108.3	110.7	109.1	109.7	106.1	106.6
3	146.6	151.1		147.5	147.7	147.4	149.6	147.8	146.3	151.4	149.0	149.1	146.2	146.6
4	144.2	138.5	113.9	146.4	146.3	146.0	148.5	146.7	145.8	139.9	149.1	148.1	147.6	
5	114.3	120.6	130.0	107.9	108.1	107.8	112.1	111.7	114.0	122.8	112.2	111.2	108.2	108.2
6	120.9	122.8	121.7	122.0	122.1	121.8	120.9	120.5	118.0	118.5	118.3	118.9	119.3	120.1
7	37.7	38.1		38.1	38.5	37.9	38.4	38.1	75.4	75.4	75.4	76.1	75.4	76.3
8	40.7	40.8		41.2	41.0	41.0	41.3	40.9	45.2	43.4	43.9	43.4	43.7	43.5
9	71.7	71.0		71.0	71.0	70.7	71.2	71.3	68.5	67.7	68.4	67.9	68.4	68.0
1′	129.3	136.5		129.5	136.7	131.2	130.7	130.4	129.5	136.1	130.2	129.6	131.1	131.0
2′	111.6	113.3	115.7	110.9	112.5	108.4	113.3	111.4	112.0	113.7	109.1	109.7	108.1	108.2
3′	146.5	151.1		146.1	151.0	147.4	149.6	146.6	144.6	151.1	149.0	149.2	147.5	147.8
4′	144.2	138.5	114.0	144.2	138.4	145.8	148.5	144.5	146.8	138.8	149.4		148.0	148.1
5′	114.1	121.3	130.0	114.3	120.4	107.8	112.3	114.1	114.5	121.7	112.9	112.7	109.8	109.8
6′	121.7	122.6	121.1	121.0	122.7	121.1	121.7	122.0	122.6	123.2	121.8	121.7	122.7	122.0
7′	34.2	34.4		34.6	34.4	34.4	34.8	34.6	35.2	34.9	35.0	34.8	35.1	35.1
8′	46.1	46.2		46.3	46.5	46.1	46.7	46.5	43.8	43.5	45.2	44.0	45.1	43.9
9′	178.1	178.2		178.2	178.0	177.9	178.5	178.7	178.9	178.0	179.2	178.2	178.7	178.0
OCH_3	55.5	55.7		55.7	55.7		56.2	55.8 55.9	55.9	55.8	55.9	55.9		
OCH_2O				100.8	100.9	100.6							100.8 101.6	101.0 101.4
$OCOCH_3$		168.8 20.5			168.7 20.6					168.7 20.5 168.9 20.5 169.7 20.9		169.8 21.1		169.8 20.9



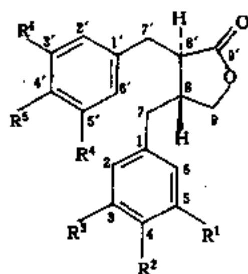


化合物 \ 取代基	R^1	R^2	R^3	R^4
24	OH	OCH_3	OCH_3	OH
25	OAc	OCH_3	OCH_3	OAc
26	OH	H	H	OH
27	OCH_2O		OCH_3	OH
28	OCH_2O		OCH_3	OAc
29	OCH_2O		OCH_2O	
30	OCH_3	OCH_3	OCH_3	OCH_3
31	OCH_3	OCH_3	OCH_3	OH

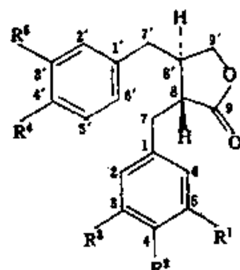
化合物 \ 取代基	R	R^1	R^2	R^3	R^4
32	OH	OH	OCH_3	OCH_3	OH
33	OAc	OAc	OCH_3	OCH_3	OAc
34	OH	OCH_3	OCH_3	OCH_3	OCH_3
35	OAc	OCH_3	OCH_3	OCH_3	OCH_3
36	OH	OCH_2O		OCH_2O	
37	OAc	OCH_2O		OCH_2O	

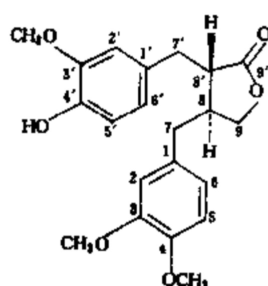
表 24-4　丁烷衍生物类木脂素 38～48 的 ^{13}C-NMR 化学位移数据[4,7,10,14,15]

C \ 化合物	**38**	**39**	**40**	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**
1	133.6	133.7	133.6	130.1	131.2	133.2	130.8	134.4	129.5	130.9	130.1
2	105.5	105.7	105.7	111.7	109.3	106.2	114.5	109.0	109.7	111.5	109.5
3	153.2	153.5	153.5	148.8	147.7	153.2	148.1	148.9	149.1	147.9	149.8
4	136.7	136.9	137.0	147.7	146.2	136.8	147.1	147.9	148.0	149.2	149.8
5	153.2	153.5	153.5	111.2	108.7	153.2	111.8	112.4	111.2	112.8	113.6
6	105.5	105.7	105.7	120.2	122.1	106.2	120.8	118.3	118.2	120.9	120.5
7	38.8	38.9	38.9	38.1	38.3	35.2	34.6	73.9	75.4	32.7	72.1
8	40.9	41.1	41.1	41.0	41.2	46.4	41.1	43.5	44.0	40.0	43.3
9	71.2	71.2	71.2	71.1	178.2	178.5	71.4	68.2	67.9	69.5	66.7
1′	129.4	130.3	136.7	133.1	131.4	131.6	129.6	130.0	130.0	138.5	139.1
2′	111.6	112.5	113.4	106.2	108.2	108.8	112.3	111.1	112.4	112.0	112.2
3′	146.7	149.2	151.3	152.9	147.7	147.9	149.3	149.2	149.0	151.3	151.7
4′	144.6	148.1	138.8	136.8	146.3	146.4	144.9		148.0	137.7	137.5
5′	114.1	111.2	121.4	152.9		108.2	112.0			120.4	118.1
6′	121.9	121.4	122.7	106.2	121.4	121.5	122.1	121.4	121.4	122.9	123.2
7′	34.4	34.6	34.6	35.0	34.8	35.2	38.2	34.7	34.3	30.8	30.7
8′	46.5	46.6	46.4	46.4	46.4	46.4	46.7	46.2	44.0	45.4	43.5
9′	178.7	178.7	178.5	178.1	71.1		179.0	179.1	178.0	177.8	177.1
OCH_3	60.7	60.9	60.9	55.8		56.1	55.9	55.8	55.9	55.9	56.3
	55.9	55.9	55.9	56.0		60.8					
		56.1	56.1	60.7							
OCH_2O					100.9	101.0					
$OCOCH_3$			168.9						169.8	169.1	168.9
			20.6						20.9	20.7	20.6



取代基 / 化合物	R^1	R^2	R^3	R^4	R^5	R^6
38	OCH_3	OCH_3	OCH_3	H	OH	OCH_3
39	OCH_3	OCH_3	OCH_3	H	OCH_3	OCH_3
40	OCH_3	OCH_3	OCH_3	H	OAc	OCH_3
41	H	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3

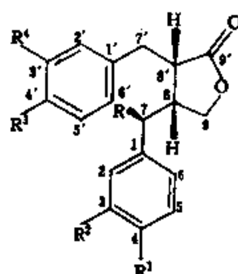




42. $R^1 = H$, $R^2 + R^3 = OCH_2O$, $R^4 + R^5 = OCH_2O$

43. $R^1 + R^2 + R^3 = OCH_3$, $R^4 + R^5 = OCH_2O$

44



取代基 / 化合物	R	R^1	R^2	R^3	R^4
45	OH	OCH_3	OCH_3	OCH_3	OCH_3
46	OAc	OCH_3	OCH_3	OCH_3	OCH_3
47	H	OCH_3	OCH_3	OAc	OCH_3
48	OAc	OCH_3	OCH_3	OAc	OCH_3

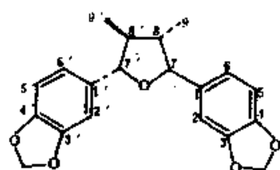
第二节　四氢呋喃类木脂素的^{13}C-NMR 化学位移

表 24-5　7，7′-单环氧木脂素 1～10 的^{13}C-NMR 化学位移数据[16～19]

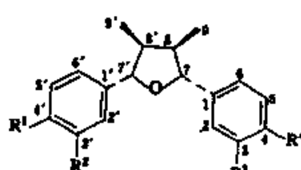
C \ 化合物	1	2	3	4	5	6	7	8	9	10
1	136.1	134.6	134.9	133.6	132.8	139.4	138.9	137.6	137.4	124.7
2	106.4	109.6	109.3	110.5	109.5	110.0	126.1	127.4	126.8	108.7
3	147.5	148.7	145.1	148.7	148.2	151.2	128.4	127.8	128.4	148.4
4	146.7	148.2	145.1	148.3	147.4	140.0	127.5	127.8	128.1	147.5
5	107.7	110.8	110.7	110.8	110.6	127.7	128.4	127.8	128.4	110.9
6	119.5	118.4	118.6	118.1	118.2	118.0	126.1	127.4	127.0	117.9
7	88.1	87.1	87.2	87.1	82.4	82.6	81.2	81.5	82.8	146.4
8	50.9	44.3	44.3	45.9	41.2	50.4	48.1	52.5	54.6	117.4
9	13.7	12.9	12.9	14.9	11.6	63.4	60.8	169.5	171.2	9.6
1′	136.1	134.6	134.9	133.2	132.8	139.4	138.9	137.6	137.2	124.7
2′	106.4	109.6	109.4	109.7	109.5	110.0	126.1	127.4	126.8	108.7
3′	147.5	148.7	145.1	148.3	148.2	151.2	128.4	127.8	128.5	148.4

续表

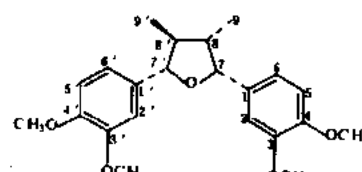
C \ 化合物	1	2	3	4	5	6	7	8	9	10
4′	146.7	148.2	145.1	147.8	147.4	140.0	127.5	127.8	128.1	147.5
5′	107.7	110.8	110.1	110.5	110.6	127.7	128.4	127.8	128.5	110.9
6′	119.5	118.4	119.3	118.4	118.2	118.0	126.1	127.4	127.0	117.9
7′	81.1	87.1	87.2	82.8	82.4	82.6	81.2	81.5	83.8	146.4
8′	50.9	44.3	44.3	47.8	41.2	50.4	48.1	52.5	55.2	117.4
9′	13.7	12.9	12.9	14.9	11.6	63.4	60.8	169.5	172.1	9.6
OCH_3		55.8	55.9	55.7	55.6	56.4				55.5
OCH_2O	100.7									
OCH_2CH_3								60.3	60.8	
								13.6	13.5	
									61.3	
									14.1	
$OCOCH_3$						168.6				
						20.6				
						170.4				
						20.6				



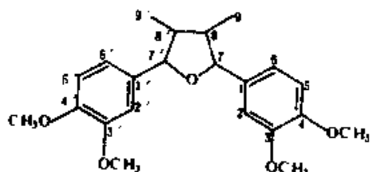
1



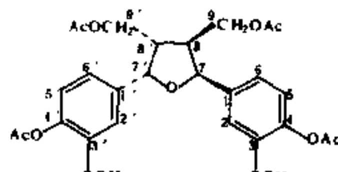
2. $R^1 = R^2 = R^3 = R^4 = OCH_3$
3. $R^1 = OH$, $R^2 = R^3 = R^4 = OCH_3$



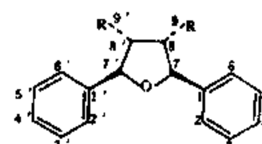
4



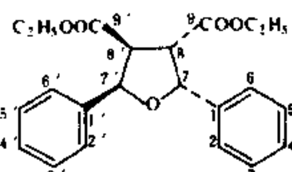
5



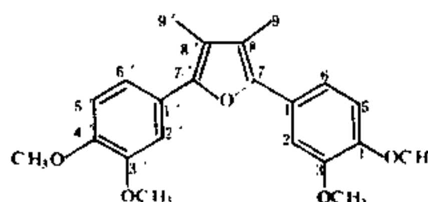
6



7. $R = CH_2OH$
8. $R = COOC_2H_5$



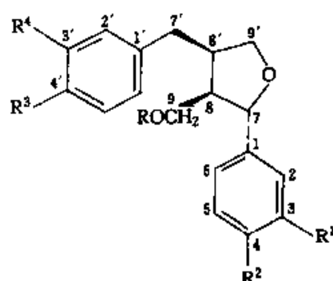
9



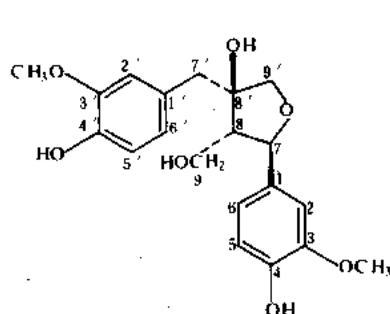
10

表 24-6　7，9′-单环氧木脂素 11～21 的 ^{13}C-NMR 化学位移数据[2,3,20,21]

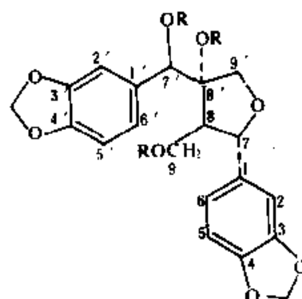
C \ 化合物	11	12	13	14	15	16	17	18	19	20	21
1	133.7	138.7	132.9	134.7	134.5	141.3	135.2	134.6		134.5	133.7
2	108.7	109.5	108.9	108.8	108.2	109.4	108.8	108.7		107.2	106.6
3	145.1	150.9	148.9	148.8	146.4	150.7	148.2	148.8		146.9	147.3
4	146.8	141.4	148.8	148.3	144.7	138.7	148.2	148.3		147.3	147.8
5	114.4	122.5	111.3	110.9	114.0	122.3	111.0	110.8		107.6	107.9
6	118.1	117.6	117.9	117.9	118.4	117.5	117.8	117.9		120.0	120.0
7	82.3	82.7	82.7	82.9	82.6	82.7	82.6	82.8	83.7	84.0	83.4
8	52.2	49.0	52.5	48.8	52.4	48.8	52.4	48.9	61.2	61.4	53.4
9	59.1	62.6	60.7	62.6	60.5	62.5	60.8	62.5	60.0	60.4	61.0
1′	131.6	138.0	135.4	132.3	132.7	132.2	132.0	138.8		136.2	129.4
2′	116.6	112.6	111.0	111.2	111.0	111.1	110.9	112.6		107.4	107.8
3′	145.1	150.9	148.2	148.3	148.6	148.7	146.4	150.7		147.0	147.6
4′	146.9	138.7	147.3	147.3	147.1	147.3	143.8	138.0		147.6	147.8
5′	114.6	122.6	111.9	111.8	111.8	111.6	114.2	122.6		108.4	108.3
6′	120.6	120.4	120.4	120.2	120.3	120.1	120.9	120.4		120.9	122.4
7′	32.3	33.4	33.2	33.1	33.0	33.0	33.2	33.4	39.9	73.2	75.2
8′	42.1	42.1	42.4	42.3	42.2	42.2	42.3	42.1	81.5	84.2	90.0
9′	72.1	72.7	72.9	72.6	72.6	72.6	72.7	72.6	77.0	75.7	73.9
OCH_3	55.1	55.8	55.9	55.8	55.7	55.7	55.8	55.8	57.8		
OCH_2O										100.8	100.9
											101.2
$OCOCH_3$		168.9		170.6		168.7		168.8			170.5
		20.6		20.8		20.5		20.6			20.7
		170.7				170.5		170.6			169.4
		20.6				20.7		20.8			21.0
											169.2
											22.2



化合物 \ 取代基	R	R^1	R^2	R^3	R^4
11	H	OCH_3	OH	OH	OCH_3
12	Ac	OCH_3	OAc	OAc	OCH_3
13	H	OCH_3	OCH_3	OCH_3	OCH_3
14	Ac	OCH_3	OCH_3	OCH_3	OCH_3
15	H	OCH_3	OH	OCH_3	OCH_3
16	Ac	OCH_3	OAc	OCH_3	OCH_3
17	H	OCH_3	OCH_3	OH	OCH_3
18	Ac	OCH_3	OCH_3	OAc	OCH_3



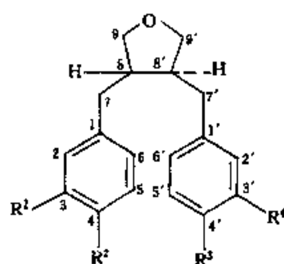
19



20. R = H
21. R = Ac

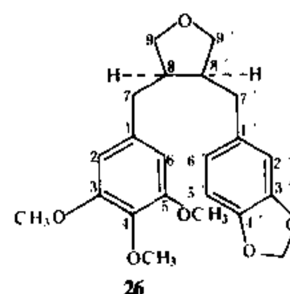
表 24-7　9，9'-单环氧木脂素 22～27 的^{13}C-NMR 化学位移数据[4,13,22,23]

C \ 化合物	22	23	24	25	26	27
1	132.9	139.8			133.9	137.7
2	113.2	106.0			107.9	111.3
3	148.3	152.9			147.5	151.2
4	145.7	127.7			145.7	139.8
5	115.6	152.9			108.8	123.0
6	121.9	106.0			121.3	120.9
7	39.8	39.8	33.9	39.9	39.2	76.6
8	47.1	47.1	43.6	43.6	46.5	48.2
9	73.5	73.5	72.0	73.2	73.2	69.9
1'	132.9	139.8			133.9	137.8
2'	113.2	106.0			107.9	119.4
3'	148.3	152.9			145.7	123.0
4'	145.7	127.7			147.5	139.8
5'	115.6	152.9			108.8	151.3
6'	121.9	106.0			121.3	113.1
7'	39.8	39.8	33.4	39.2	39.2	33.7
8'	47.1	47.1	43.8	46.3	46.5	50.0
9'	73.5	73.8	71.9	73.2	73.7	102.9
OCH_3						56.0
OCH_2O					100.7	
$OCOCH_3$						169.2
						20.7

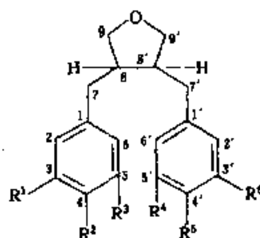


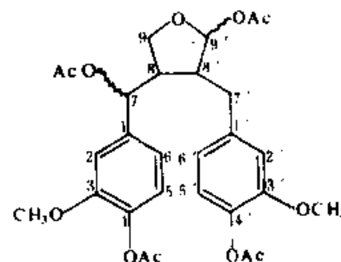
22. $R^1 = R^4 = OCH_3$，$R^2 = R^3 = OH$

25. $R^1 + R^2 = OCH_2O$，$R^3 + R^4 = OCH_2O$



26





23. $R^1 = R^3 = R^4 = R^6 = OCH_3$，$R^2 = R^5 = OAc$

24. $R^1 = R^2 = R^3 = OCH_3$，$R^4 = H$，$R^5 + R^6 = OCH_2O$

27

第三节　二苯基四氢呋喃并四氢呋喃类木脂素的^{13}C-NMR 化学位移

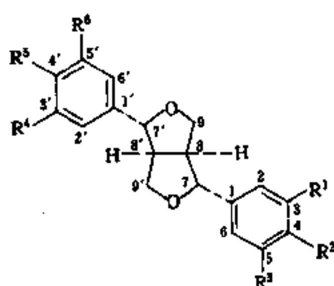
表 24-8　二苯基四氢呋喃并四氢呋喃类木脂素 1～12 的^{13}C-NMR 化学位移数据[3,22,24～27]

C \ 化合物	1①	2	3	4	5	6	7	8	9	10	11①	12
1	133.8	132.0	139.8	133.3	133.2	134.0	134.0	134.9	134.9	136.6	133.1	134.9
2	128.3	108.8	109.6	109.0	109.1	109.7	109.1	106.3	106.3	102.8	104.5	106.4
3	116.1	146.8	150.9	148.9	149.0	149.5	148.8	146.8	146.9	153.3	148.8	146.4
4	157.7	145.2	138.9	148.4	148.4	148.8	149.5	147.7	147.7	137.5	136.1	147.8
5	116.1	114.4	122.5	110.8	110.9	111.4	111.4	107.9	107.9	153.3	148.8	108.1
6	128.3	118.5	117.7	118.6	118.1	118.4	118.4	119.1	119.1	102.8	104.5	119.2
7	86.7	85.7	85.3	85.6	85.6	85.8	85.8	85.6	85.6	85.9	86.7	85.7
8	55.0	53.7	54.2	54.0	54.0	54.3	54.3	54.2	54.2	54.4	55.0	54.3
9	64.5	71.3	71.8	71.5	71.7	71.7	71.7	71.5	71.6	71.9	64.5	71.6
1'	133.8	132.0	139.8	132.6	140.4	134.0	134.0	139.9	133.4	136.6	133.1	136.7

续表

C \ 化合物	1①	2	3	4	5	6	7	8	9	10	11①	12
2′	128.3	108.8	109.6	108.4	109.7	109.7	109.1	106.3	109.1	102.8	104.5	102.8
3′	116.1	146.8	150.9	146.5	151.0	149.5	148.8	146.8	148.4	153.3	148.8	153.3
4′	157.7	145.2	138.9	145.0	138.9	148.8	149.5	147.7	149.0	137.5	136.1	137.4
5′	116.1	114.2	122.5	114.1	122.5	111.4	111.4	108.0	110.9	153.3	148.8	153.3
6′	128.3	118.5	117.7	118.7	117.7	118.4	118.4	119.1	118.1	102.8	104.5	102.8
7′	86.7	85.7	85.3	85.6	85.4	85.8	85.8	85.6	85.7	85.9	86.7	85.9
8′	55.0	53.7	54.3	54.0	54.3	54.3	54.3	54.2	54.1	54.4	55.0	54.3
9′	64.5	71.3	71.8	71.5	71.7	71.7	71.7	71.5	71.6	71.9	64.5	71.9
OCH_3		55.6	55.8	55.8	55.8	55.6 55.9	55.6 55.9		55.8	56.2 60.8		56.1 60.8
OCH_2O			1					100.9	100.9			101.0
$OCOCH_3$			168.8 20.5		168.8 20.5							

① 化合物Ⅰ，Ⅱ在 $D_2O+CD_3COCD_3$ 中测定。

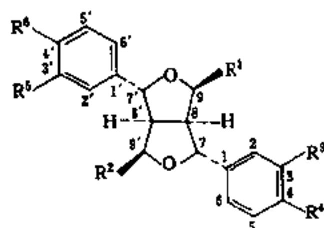


化合物 \ 取代基	R^1	R^2	R^3	R^4	R^5	R^6
1	H	OH	H	H	OH	H
2	OCH_3	OH	H	OCH_3	OH	H
3	OCH_3	OAc	H	OCH_3	OAc	H
4	OCH_3	OCH_3	H	OCH_3	OH	H
5	OCH_3	OCH_3	H	OCH_3	OAc	H
6	OCH_3	OCH_3	H	OCH_3	OCH_3	H
7	OCH_3	OCH_3	H	OCH_3	OCH_3	H
8	OCH_2O		H	OCH_2O		H
9	OCH_2O		H	OCH_3	OCH_3	H
10	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3
11	OCH_3	OH	OCH_3	OCH_3	OH	OCH_3
12	OCH_2O		H	OCH_3	OCH_3	OCH_3

表 24-9 二苯基四氢呋喃并四氢呋喃类木脂素 13~23 的 ^{13}C-NMR 化学位移数据[21,28]

C \ 化合物①	13	14	15	16	17	18	19	20	21	22	23
1	135.4	135.1	134.2	139.3	133.4	139.1	136.5	134.7	135.9	133.8	135.0
2	106.3	106.1	110.8	110.9	110.5	111.1	107.3	106.3	110.4	109.7	110.1
3	147.2	147.2	145.8	151.4	146.3	151.1	147.2	147.6	148.2	148.5	148.5
4	148.1	148.1	147.5	141.1	147.8	141.5	147.9	148.2	148.9	148.9	149.1
5	108.1	108.1	114.9	122.8	115.2	122.8	107.9	108.2	111.5	111.6	111.6
6	119.2	119.2	118.9	118.3	119.3	118.5	119.0	119.8	118.6	118.5	118.9
7	83.0	83.3	84.2	85.0	84.8	84.2	85.3	85.9	84.2	85.1	84.7
8	62.1	61.1	60.9	58.5	59.2	59.1	60.4	58.5	60.9	58.2	59.2
9	101.0	101.1	100.2	101.1	107.1	107.5	101.2	100.3	100.4	100.4	107.1
1′	136.1	135.5	134.2	139.3	134.4	139.1	136.5	134.7	135.9	133.8	135.0
2′	107.1	106.6	110.8	110.9	110.5	111.1	107.3	106.3	110.4	109.7	110.1
3′	147.3	147.3	145.8	151.4	146.3	151.1	147.9	147.6	148.2	148.5	148.5
4′	148.1	148.1	147.5	141.1	147.8	141.5	147.9	148.2	148.9	148.9	149.1
5′	108.2	108.3	114.9	122.8	115.2	122.8	107.9	108.2	111.5	111.6	111.6
6′	120.0	119.8	118.9	118.3	119.3	118.5	119.0	119.8	118.6	118.5	118.9
7′	88.1	89.0	84.2	85.0	84.8	84.2	85.3	85.9	84.2	85.1	84.7
8′	53.2	52.6	60.9	58.5	59.2	59.1	60.4	58.5	60.9	58.2	59.2
9′	72.3	72.5	100.2	101.1	107.1	107.5	101.2	100.3	100.4	100.4	107.1
OCH_3			55.5	55.8	54.3 55.4	54.5 55.9			55.4 55.6	55.3 55.6	54.3 55.3 55.6
OCH_2O	101.1	101.1					101.0	101.0			
$OCOCH_3$		170.3 21.3		169.1 20.3 170.1 20.9		169.4 20.3		169.7 21.2		169.4 21.0	

① 化合物 15~18 在 $(CD_3)_2SO$ 中测定。

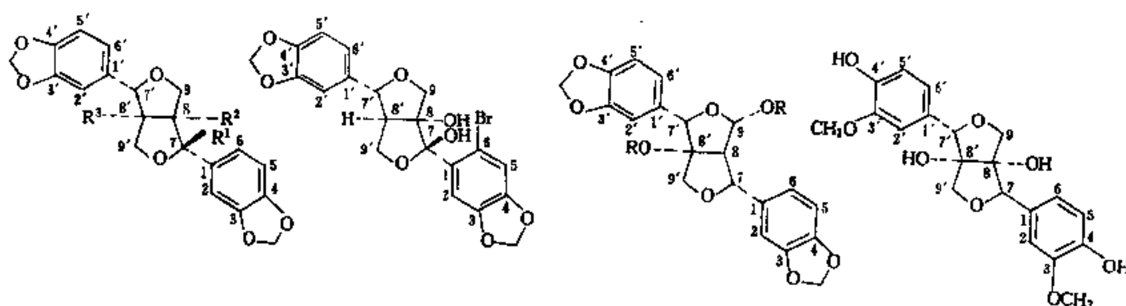


化合物 \ 取代基	R¹	R²	R³	R⁴	R⁵	R⁶
13	OH	H	OCH_2O		OCH_2O	
14	OAc	H	OCH_2O		OCH_2O	
15	OH	OH	OCH_3	OH	OCH_3	OH
16	OAc	OAc	OCH_3	OAc	OCH_3	OAc
17	OCH_3	OCH_3	OCH_3	OH	OCH_3	OH
18	OCH_3	OCH_3	OCH_3	OAc	OCH_3	OAc
19	OH	OH	OCH_2O		OCH_2O	
20	OAc	OAc	OCH_2O		OCH_2O	
21	OH	OH	OCH_3	OCH_3	OCH_3	OCH_3
22	OAc	OAc	OCH_3	OCH_3	OCH_3	OCH_3
23	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3

表 24-10 二苯基四氢呋喃并四氢呋喃类木脂素 24~32 的 ^{13}C-NMR 化学位移数据[4,21,24,29~33]

C \ 化合物	24	25	26	27	28	29	30	31	32①
1	129.4	130.1	135.0	133.8	129.7	129.9	129.5	130.0	128.4
2	108.2	108.1	108.2	106.8	106.2	106.3	107.5	108.1	112.2
3	147.3	147.2	147.9	147.1	147.2	147.1	147.9	147.5	145.8
4	148.2	147.9	148.3	147.5	147.7	147.8	147.9	147.8	146.8
5	108.6	108.7	108.3	107.8	107.5	107.6	108.3	109.2	114.5
6	120.1	122.2	120.1	119.5	119.2	119.5	120.2	123.0	120.1
7	87.5	86.7	102.7	101.5	83.4	83.7	86.9	86.8	86.9
8	91.7	97.1	95.0	94.1	66.0	64.7	87.5	92.3	87.5
9	71.6	69.8	76.8	76.3	101.0	100.2	76.4	74.3	74.5
1′	134.8	133.9	135.0	134.8	135.1	133.9	129.5	130.0	128.4
2′	106.9	106.7	106.8	107.5	108.1	108.1	107.5	108.1	112.2
3′	147.3	147.4	147.9	147.4	147.7	147.3	147.9	147.5	145.8
4′	148.2	147.9	148.3	147.6	148.0	147.5	147.9	147.8	146.8
5′	107.5	107.8	107.2	112.0	108.4	109.3	108.3	109.2	114.5
6′	119.8	119.7	119.6	111.6	120.1	123.4	120.2	123.0	120.1
7′	85.9	85.7	90.1	87.7	88.0	88.8	86.9	86.8	86.9
8′	60.6	58.9	60.3	59.6	92.0	94.6	87.6	92.3	87.5
9′	75.0	75.1	68.6	69.0	75.1	75.8	76.4	74.3	74.5
OCH_3									55.5
OCH_2O	101.1	100.9	101.3	100.9	101.0	101.0	101.1	100.2	
	101.2	101.0	101.5	101.6	101.2				
$OCOCH_3$		169.2				169.0		169.0	
		20.9				20.7		20.9	
						169.7			
						21.2			

① 化合物 32 在 $(CD_3)_2SO$ 中测定。



24. $R^1 = R^3 = H$, $R^2 = OH$
25. $R^1 = R^3 = H$, $R^2 = OAc$
26. $R^1 = R^2 = OH$, $R^3 = H$
30. $R^1 = H$, $R^2 = R^3 = OH$
31. $R^1 = H$, $R^2 = R^3 = OAc$

27

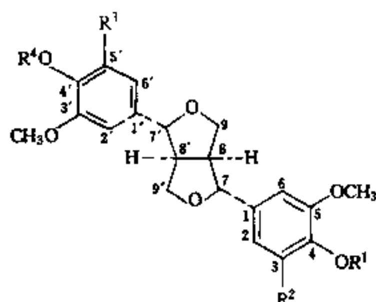
28. R = H
29. R = Ac

32

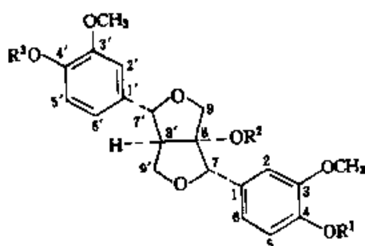
表 24-11　二苯基四氢呋喃并四氢呋喃类木脂素 33～43 的 ^{13}C-NMR 化学位移数据[34～36]①

C \ 化合物	33	34	35	36	37	38	39	40	41	42	43
1	135.2	137.8	135.2	133.9	130.3	130.2	131.1	131.1	133.1	133.1	133.1
2	110.4	110.7	110.5	104.3	110.7	110.1	110.7	110.2	109.9	109.6	110.1
3	145.9	145.7	148.9	152.7	146.3	146.2	145.9	145.9	146.2	146.0	146.1
4	148.9	151.3	148.9	137.2	148.2	148.3	147.4	148.7	151.1	148.9	150.3
5	110.4	118.8	110.5	152.7	114.6	114.6	114.6	112.5	111.4	113.8	118.3
6	120.3	120.3	118.6	104.3	119.0	118.5	118.8	118.4	119.0	119.7	120.6
7	85.1	85.6	84.8	85.1	86.1	86.0	86.9	86.9	87.5	86.8	86.7
8	53.5	54.3	53.5	53.6	97.0	96.9	91.2	91.2	91.9	97.2	97.1
9	70.9	72.0	71.0	71.3	73.8	73.7	74.7	74.7	74.9	74.9	74.9
1′	132.1	140.2	133.8	133.9	131.2	131.7	132.3	133.9	132.2	132.4	139.1
2′	110.4	110.0	109.8	104.3	113.0	111.6	112.5	111.6	111.2	111.0	113.7
3′	145.9	150.9	145.8	152.7	147.5	148.1	147.4	148.3	149.3	148.9	151.3
4′	148.9	139.2	148.1	137.2	148.2	148.7	148.3	148.7	148.9	150.3	139.4
5′	115.1	122.1	111.6	152.7	115.3	112.9	115.1	114.6	111.4	118.6	119.7
6′	118.1	117.9	118.6	104.3	121.1	121.0	119.7	119.7	120.3	120.5	122.9
7′	84.8	85.6	84.8	85.1	84.5	84.3	85.4	85.1	71.7	72.5	72.5
8′	53.5	54.5	53.5	53.6	58.2	58.2	60.8	60.8	60.3	58.7	58.9
9′	70.9	72.0	71.0	71.3	69.7	60.7	70.3	70.3	85.8	85.6	85.4
OCH_3	55.6	56.0	55.4	56.4	55.6	55.4	55.6	55.7	55.9	55.9	55.9
		56.2	55.6		55.8	55.7		55.9	56.2	56.1	56.1
$OCOCH_3$		169.1			168.8	168.7			169.4	169.3	169.0
		20.7			20.6	20.5				20.5	20.5
		169.4							170.3	170.1	169.3
		20.7								20.7	20.5
		170.3							170.6	170.4	170.2
		20.7								20.7	20.5
		170.6									170.5
		20.7									20.5

① 化合物 33，35～40 在 $(CD_3)_2SO$ 中测定。



33. R^1 = Glu，$R^2 = R^3 = R^4$ = H
34. R^1 = Glu $(OAc)_4$，$R^2 = R^3 = R^4$ = H
35. R^1 = Glu，$R^2 = R^3$ = H，$R^4 = CH_3$
36. $R^1 = R^4$ = Glu，$R^2 = R^3 = OCH_3$

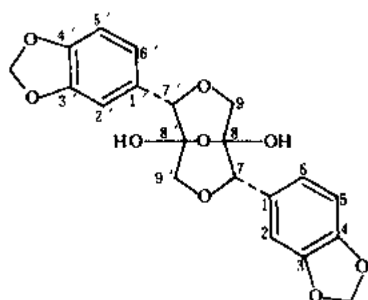


37. R^1 = Glu，R^2 = Ac，R^3 = H
38. R^1 = Glu，R^2 = Ac，$R^3 = CH_3$
39. R^1 = Glu，$R^2 = R^3$ = H
40. R^1 = Glu，R^2 = H，$R^3 = CH_3$
41. R^1 = Glu $(OAc)_4$，R^2 = H，$R^3 = CH_3$
42. R^1 = Glu $(OAc)_4$，R^2 = Ac，$R^3 = CH_3$
43. R^1 = Glu $(OAc)_4$，$R^2 = R^3$ = Ac

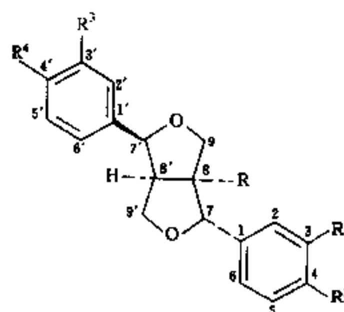
表 24-12　二苯基四氢呋喃并四氢呋喃类木脂素 44～56 的 ^{13}C-NMR 化学位移数据[4,24,34,37～39]

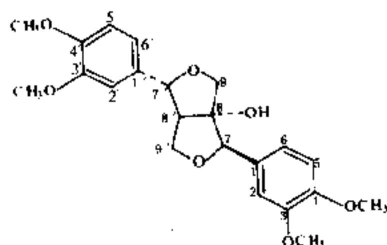
C \ 化合物	44①	45	46	47	48	49	50	51	52	53	54	55①	56
1	131.4	133.1	130.4	135.3	130.7	132.9	133.7	130.0	130.6	133.1	140.3	132.4	131.2
2	107.8	109.1	108.5	108.1	110.5	109.7	106.7	107.2	107.1	109.1	110.0	110.5	109.5
3	147.2	146.8	144.8	147.2	148.3	149.2	148.0	147.6	147.5	148.9	151.3	145.9	146.0
4	147.3	145.4	146.5	147.6	149.4	149.5	148.3	148.3	148.2	148.1	139.2	145.9	147.7
5	108.5	111.2	114.4	106.3	111.5	111.3	108.2	108.1	108.2	111.2	122.7	115.2	115.3
6	121.5	119.2	119.5	119.5	119.2	118.7	119.6	120.0	120.0	119.2	118.1	118.5	118.2
7	82.3	87.8	87.7	87.6	88.8	85.2	102.8	105.2	105.0	87.8	87.4	81.1	81.3
8	94.9	54.5	54.6	54.6	57.4	62.7	94.8	95.6	95.5	54.5	54.6	49.2	49.3
9	68.6	71.1	71.1	69.6	68.4	69.7	76.8	76.6	76.6	71.1	71.1	68.7	69.0
1′	131.4	131.0	135.3	132.3	128.1	129.7	135.3	135.2	135.2	131.0	131.0	132.6	135.4
2′	107.8	108.6	106.5	106.5	109.2	108.8	107.1	107.4	107.2	108.6	109.1	110.5	110.5
3′	147.2	148.9	148.0	146.5	148.3	148.7	148.0	147.9	147.8	146.8	148.9	145.9	148.5
4′	108.5	148.1	147.2	147.9	149.1	149.0	148.3	148.1	148.0	145.4	148.1	145.9	149.0
5′	121.5	114.3	108.2	108.1	111.4	111.4	108.2	108.2	108.2	114.3	111.2	115.3	116.0
6′	82.3	117.8	118.5	118.7	117.7	117.5	120.7	120.5	120.3	117.8	117.8	117.7	117.7
7′	94.9	82.1	82.1	82.0	81.2	88.7	90.0	90.0	90.0	82.1	82.1	86.8	86.7
8′	68.6	50.2	50.2	50.1	90.8	93.9	60.2	60.4	60.5	50.2	50.2	53.6	54.0
9′		69.7	69.7	70.9	75.9	76.8	68.5	68.5	68.5	69.7	69.8	70.4	70.4
OCH_3		55.9	56.0		55.6	56.0		49.0		55.9	55.9	55.7	55.7
												55.8	
OC_2H_5									57.4				
									15.3				
OCH_2O	100.9		101.0	101.0			101.3	101.2	101.1				
							101.4	101.3	101.3				
$OCOCH_3$												169.1	
												20.7	

① 化合物 44 在 $CDCl_3$ + $(CD_3)_2SO$ 中测定；化合物 55 在 $(CD_3)_2SO$ 中测定。



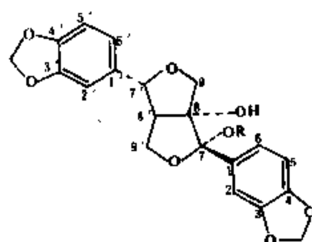
44



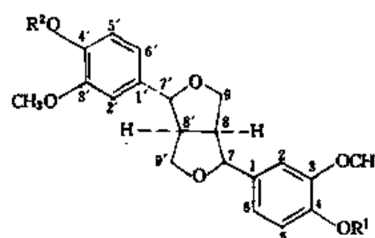


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化合物 \ 取代基	R	R1	R2	R3	R4
45	H	OCH_3	OCH_3	OCH_3	OCH_3
46	H	OH	OCH_3	OCH_2O	
47	H	OCH_2O		OCH_2O	
48	OH	OCH_3	OCH_3	OCH_3	OCH_3
53	H	OCH_3	OH	OCH_3	OCH_3
54	H	OCH_3	OAc	OCH_3	OCH_3



50. R = H
51. R = CH_3
52. R = C_2H_5

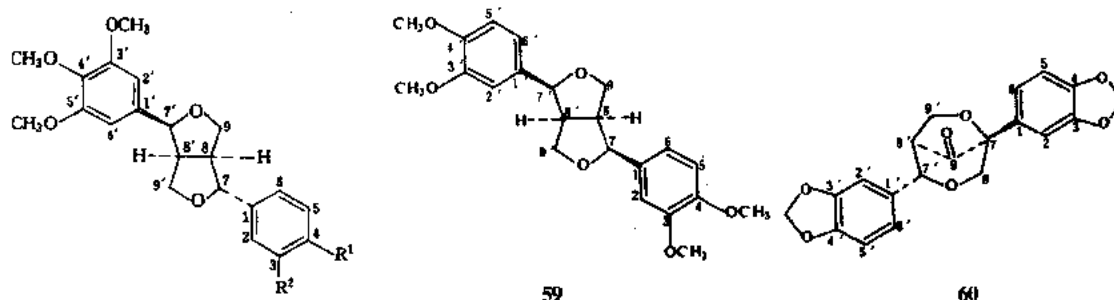


55. R^1 = Glu, R^2 = H
56. R^1 = H, R^2 = Glu

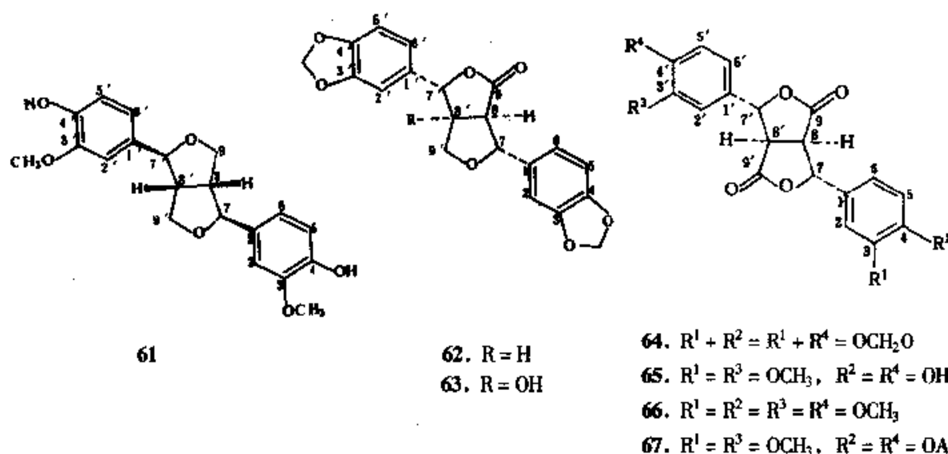
表 24-13 二苯基四氢呋喃并四氢呋喃类木脂素 57～67 的 ^{13}C-NMR 化学位移数据[19,20,24,25,39,40]

C \ 化合物	57	58	59	60	61	62	63	64	65①	66①	67①
1	135.2	133.7	131.4	127.4	131.2	132.8	128.9	131.7	129.0	130.5	137.2
2	106.6	109.3	109.6	108.3	107.9	105.6	106.6	105.6	110.6	110.0	110.8
3	147.3	148.8	147.0	147.7	146.8	147.1	146.8	148.3	147.7	146.3	151.3
4	148.0	149.3	148.7	148.6	145.5	148.2	147.2	148.4	147.9	149.4	139.8
5	108.2	111.2	110.9	108.6	114.5	108.2	107.9	108.6	115.5	111.7	123.3
6	119.5	118.5	118.4	119.6	118.1	118.6	119.7	119.0	119.1	118.8	118.3
7	87.7	87.6	83.9	81.4	83.5	84.3	82.6	81.9	82.1	81.7	81.2
8	54.6	54.5	49.5	77.2	50.0	49.9	58.8	48.2	48.1	48.1	47.6
9	71.1	71.1	68.7	204.7	188.0	176.4	174.9	174.9	175.4	175.3	175.1
1′	134.1	134.2	131.4	130.6	132.4	134.2	134.6	131.7	129.0	130.5	137.2
2′	102.8	102.8	109.6	106.9	108.2	105.8	107.6	105.6	110.6	110.0	110.8
3′	153.3	153.3	147.0	147.9	147.0	147.8	146.9	148.3	147.4	146.3	151.3
4′	137.1	137.1	148.7	148.6	146.2	148.2	147.4	148.4	147.9	149.4	139.8
5′	153.3	153.3	110.9	107.1	114.8	108.4	108.0	108.6	115.5	111.7	123.3
6′	102.8	102.8	118.4	120.2	118.5	118.9	121.2	119.0	119.1	118.8	118.3
7′	82.2	82.2	83.9	85.2	72.8	83.2	85.6	81.9	82.1	81.7	81.2
8′	50.1	50.1	49.5	50.0	53.4	53.2	86.2	48.2	48.1	48.1	47.9
9′	69.8	69.7	68.7	67.5	84.6	72.6	77.2	74.9	175.4	175.3	175.1
OCH_3	56.2 60.9	56.2 56.0 60.9	55.8		56.1				55.8	55.6 55.7	56.0
OCH_2O	101.1			101.2 101.4		101.0 101.3	101.0	101.5			
$OCOCH_3$											168.4 20.3

① 化合物 65～67 在 $(CD_3)_2SO$ 中测定。



57. $R^1 + R^2 = OCH_2O$
58. $R^1 = OCH_3$, $R^2 = OCH_3$



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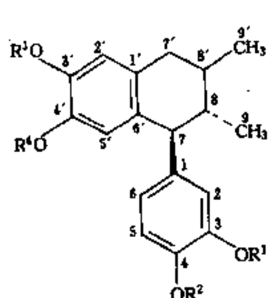
62. R = H
63. R = OH

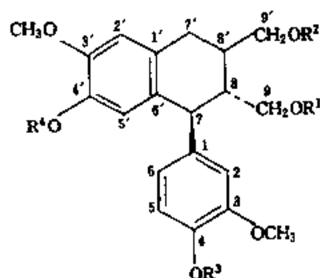
64. $R^1 + R^2 = R^1 + R^4 = OCH_2O$
65. $R^1 = R^3 = OCH_3$, $R^2 = R^4 = OH$
66. $R^1 = R^2 = R^3 = R^4 = OCH_3$
67. $R^1 = R^3 = OCH_3$, $R^2 = R^4 = OAc$

第四节 4-苯基四氢萘类木脂素的 ^{13}C-NMR 化学位移

表 24-14 4-苯基四氢萘类木脂素 1~13 的 ^{13}C-NMR 化学位移数据[1~3,41,42]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13
1	132.5	133.4	132.1	132.6	138.4	131.7	131.0	132.8	131.7	131.9	138.4	132.1	138.6
2	112.3	112.0	112.7	112.0	113.1	112.8	112.5	112.5	111.9	112.6	113.1	112.4	113.1
3	149.0	147.3	147.5	145.2	151.0	148.9	148.9	149.1	149.1	146.4	150.9	148.9	151.3
4	147.0	147.3	147.3	143.5	142.7	146.9	147.1	145.8	147.8	144.1	143.4	147.1	143.0
5	110.8	110.7	110.5	114.5	122.7	110.8	111.0	111.5	111.1	114.3	122.7	111.0	122.7
6	122.0	121.6	122.6	121.9	121.5	121.7	121.6	121.1	121.7	121.6	121.5	121.8	121.7
7	54.4	54.1	54.2	47.4	47.2	48.0	47.3	47.7	47.0	47.0	47.6	47.3	46.8
8	43.9	43.6	44.0	47.5	43.5	48.2	43.7	48.0	43.4	47.0	43.8	44.9	44.1
9	17.2	16.7	17.1	62.1	63.0	62.6	63.4	62.4	63.1	61.3	63.4	71.4	67.1
1′	129.1	129.8	132.1	127.2	134.0	128.1	127.5	127.7	133.8	128.3	127.7	128.9	134.3
2′	110.8	109.4	107.5	110.6	111.7	110.7	110.7	111.0	111.7	110.6	110.8	111.1	111.9
3′	147.2	144.3	145.6	147.1	149.2	147.3	147.6	147.6	149.1	147.0	147.4	147.2	149.3
4′	147.4	144.3	145.6	144.1	137.9	147.0	147.1	144.0	137.8	146.5	147.3	147.5	137.9
5′	113.0	107.5	109.1	115.8	123.6	111.9	111.9	116.3	123.5	111.8	112.6	112.9	123.5
6′	139.1	138.9	140.4	136.8	131.0	137.6	136.6	138.4	135.9	136.5	130.4	138.1	131.5
7′	39.1	39.4	39.0	32.8	33.1	33.2	32.7	33.2	33.1	32.4	32.7	33.1	33.1
8′	35.6	35.5	35.4	39.5	35.2	39.9	35.4	39.9	35.3	38.9	35.5	36.4	34.6
9′	20.0	20.3	20.0	65.7	66.2	66.2	66.4	66.0	66.3	65.0	66.4	75.4	65.9
OCH_3	55.9	54.5	54.2	55.6	55.9	55.7	55.8	56.0	56.4	55.1	55.9	55.8	56.1
	55.8	55.8	55.8									58.9	
OCH_2O		100.3	100.8										
$OCOCH_3$					170.8		170.8		171.4		170.9		171.1
					20.8		20.9		21.4		20.9		20.7
					170.6		170.7		171.2		170.7		168.9
					20.8		20.9		21.4		20.9		20.7
					169.0				199.5		168.4		169.7
					20.8				21.1		20.9		20.7
					168.8								169.9
					20.8								20.7





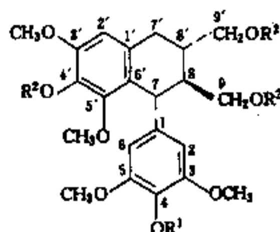
3. $R^1 + R^2 = CH_2$, $R^3 = R^4 = CH_3$
4. $R^1 = R^2 = R^3 = R^4 = H$
5. $R^1 = R^2 = R^3 = R^4 = Ac$
6. $R^1 = R^2 = H$, $R^3 = R^4 = CH_3$
7. $R^1 = R^2 = Ac$, $R^3 = R^4 = CH_3$
8. $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$
9. $R^1 = R^2 = R^4 = Ac$, $R^3 = CH_3$
10. $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$
11. $R^1 = R^2 = R^3 = Ac$, $R^4 = CH_3$
12. $R^1 = R^2 = R^3 = R^4 = CH_3$
13. $R^1 = Xyl\ (OAc)_3$, $R^2 = R^3 = R^4 = Ac$

1. $R^1 = R^2 = R^3 = R^4 = CH_3$
2. $R^1 = R^2 = CH_3$, $R^3 + R^4 = CH_2$

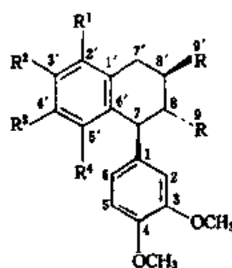
表 24-15 4-苯基四氢萘类木脂素 14～23 的 ^{13}C-NMR 化学位移数据[1,3,20,41～43]

C \ 化合物	14①	15	16	17	18	19	20①	21	22①	23
1	137.6	144.9	132.0	131.8	131.9		137.4	145.1	135.5	138.5
2	106.0	105.0	112.1	112.0	109.4		106.0	105.0	106.4	108.8
3	147.4	151.9	148.6	148.6	145.9		147.4	151.9	147.3	147.1
4	133.3	127.3	146.8	147.1	147.8		133.3	127.0	133.5	147.1
5	147.4	151.9	110.9	110.8	107.7		147.4	131.9	147.5	110.8
6	106.0	105.0	119.9	120.5	122.7		106.0	105.0	106.4	119.4
7		43.0	45.3	45.4	47.3	44.8		42.5	46.7	50.8
8	46.6	44.4	41.4	41.9	45.1	47.6	44.5	45.0	43.4	41.9
9	62.3	63.1	73.6	71.9	71.2	60.5	69.0	68.2	67.9	18.6
1′	128.5	135.2	135.6	115.1	129.0		128.5	135.4	126.9	126.9
2′	106.6	106.9	102.9	106.7	111.2		106.6	106.8	111.5	112.7
3′	146.3	151.3	147.5	147.2	147.1		146.4	151.4	145.3	148.4
4′	137.1	137.7	139.9	133.4	147.3		137.1	131.7	143.8	147.3
5′	146.8	150.9	141.9	142.1	113.1		146.7	150.8	115.9	110.8
6′	124.9	124.3	124.8	138.1	139.7		124.9	124.3	131.7	127.1
7′	32.2	33.6	33.4	33.3	33.2	40.1	32.5	33.5	32.2	120.9
8′		35.5	37.0	36.1	36.3	73.4	38.8	35.3	38.3	137.9
9′	64.6	66.3	76.1	75.5	75.3	69.4	65.6	66.2	65.5	22.1
OCH_3	55.6	56.0	55.8	55.8	55.8	56.0	55.6	56.0	55.3	55.7
	56.1	56.2	55.9	55.9	55.9		56.0	56.3	55.8	
	56.1	60.1	59.0	56.4	58.9		58.9	60.0		
	58.9		58.9	58.9						
OCH_2O	•		100.6	101.1	100.8					

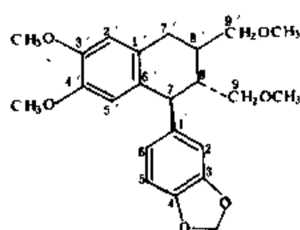
① 化合物 14，20，22 在 $(CD_3)_2SO$ 中测定。



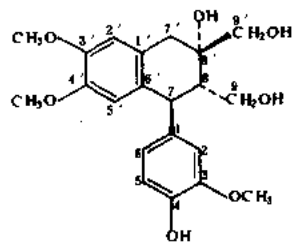
14. $R^1 = R^2 = H$
15. $R^1 = R^2 = Ac$
20. $R^1 = Glu$, $R^2 = H$
21. $R^1 = Glu\ (OAc)_4$, $R^2 = H$



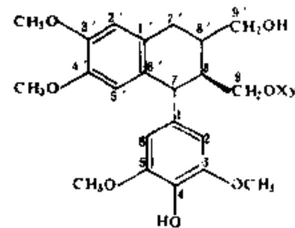
16. $R = CH_2OCH_3$, $R^1 = H$, $R^4 = OCH_3$, $R^2 + R^3 = OCH_2O$
17. $R = CH_2OCH_3$, $R^1 = H$, $R^2 = OCH_3$, $R^1 + R^4 = OCH_2O$
23. $R = CH_3$, $R^1 = R^4 = H$, $R^2 = R^3 = OCH_3$



18



19



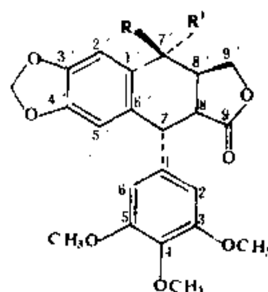
22

第五节 4-苯基四氢萘并丁内酯类木脂素的^{13}C-NMR 化学位移

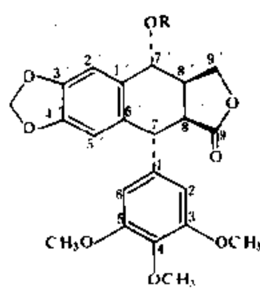
表 24-16 4-苯基四氢萘并丁内酯类木脂素 1～11 的^{13}C-NMR 化学位移数据[13,44,45]

C \ 化合物	1	2	3	4	5	6	7	8	9①	10	11
1	136.0	135.4	134.6	134.9	134.1	139.1	138.8	131.9	134.8	140.9	138.6
2	108.1	108.1	108.0	108.1	107.7	105.6	106.3	107.5	112.7	112.0	113.1
3	152.3	152.1	152.0	152.3	152.2	153.2	153.3	152.8	148.6	151.8	151.4
4	136.9	136.6	137.0	136.9	137.1	136.6	136.6	137.4	146.0	139.3	139.0
5	152.3	152.2	152.0	152.3	152.2	153.3	153.0	152.8	115.8	123.3	123.2
6	108.1	108.1	108.0	108.1	107.7	106.3	106.3	107.5	121.8	120.7	120.9
7	44.5	44.0	43.6	43.8	43.5	43.8	44.4	44.5	48.2	47.6	46.6
8	46.5	45.0	45.6	40.4	41.2	45.4	45.4	46.5	42.5	41.7	41.2
9	172.7	174.6	173.2	174.9	173.8	178.0	176.7	172.7	72.9	71.7	71.2
1′	128.1	133.1	128.1	131.7	127.3	132.8	126.2	128.0	126.6	133.8	133.9
2′	108.1	106.2	106.8	108.9	109.2	104.8	109.8	105.5	111.9	113.1	112.1
3′	146.8	147.2	147.3	148.2	148.4	146.6	147.2	147.8	147.2	150.0	149.9
4′	146.5	147.2	147.8	147.2	147.0	146.5	148.4	152.9	145.2	138.6	138.0
5′	110.3	109.3	109.4	110.2	110.1	108.5	108.3	110.2	116.5	123.8	121.9
6′	130.5	130.6	132.1	131.7	132.4	130.3	131.3	141.3	132.4	130.6	131.4
7′	33.1	72.1	73.4	66.5	67.8	68.3	72.4	188.0	29.6	29.7	28.4
8′	32.7	40.0	38.6	38.3	36.4	42.6	29.8	43.3	50.2	50.0	38.6
9′	72.0	71.3	71.1	67.6	67.1	69.7	70.5	66.8	179.2	176.6	179.1
OCH_3	56.2	56.0	56.0	56.1	56.1	56.4	56.0	56.1	56.2	56.0	55.8
OCH_3	60.6	60.5	60.5	60.6	60.6	60.3	60.7	60.6			
OCH_2O	101.0	101.1	101.4	101.3	101.5	101.2	102.0	102.2			
$OCOCH_3$			171.0		170.0		170.0			169.0	168.9
			20.9		20.8		20.8			20.7	20.7

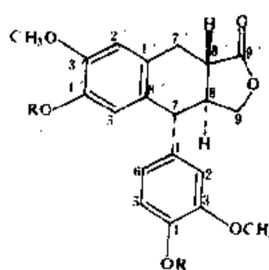
① 化合物 9 在 CD_3OD 中测定。



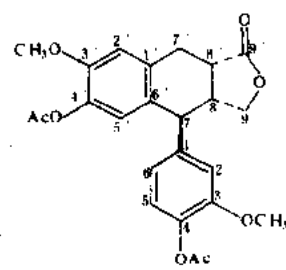
1. R = R^1 = H
2. R = H, R^1 = OH
3. R = H, R^1 = OAc
4. R = OH, R^1 = H
5. R = OAc, R^1 = H
8. R = R^1 = O



6. R = H
7. R = Ac



9. R = H
10. R = Ac

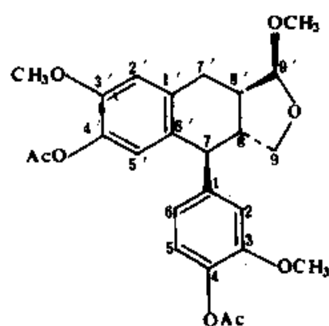


11

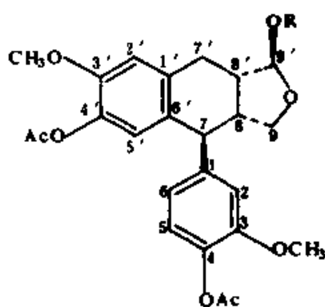
表 24-17　4-苯基四氢萘并丁内酯类木脂素 12～23 的^{13}C-NMR 化学位移数据[4,20,45,46]①

化合物 / C	12	13	14	15	16	17	18	19	20	21	22	23
1	142.6	140.1	140.4		145.0	131.4	131.2	131.2	144.2	144.1	144.4	144.6
2	112.0	113.4	113.7		105.8	109.7	115.0	114.5	106.1	106.1	106.3	106.1
3	151.2	151.2	151.4		146.7	146.6	147.4	145.1	147.5	147.5	147.5	147.5
4	138.6	138.0	139.9		146.9	147.0	148.9	148.8	147.5	147.5	147.5	147.5
5	122.8	121.0	121.7		107.7	116.7	116.5	116.5	108.2	108.2	108.1	108.1
6	120.6	121.4	121.3		123.7	120.7	120.6	120.7	123.7	123.6	123.6	123.5
7	49.1	47.5	47.6	48.5	118.7	125.7	121.6	121.6	119.2		119.2	119.4
8	49.5	45.8	46.0	45.1	121.7	128.5	130.9	130.8	126.9	126.0	127.0	123.6
9	70.9	70.6	70.8	70.3	169.6	170.4	168.4	168.4	169.9	169.7	169.7	169.8
1′	134.9	136.0	136.1		129.7	130.5	129.1	126.4	130.7	130.7	131.0	130.7
2′	112.8	111.7	111.8		101.0	107.8	112.7	112.7	130.8	100.8	105.1	104.9
3′	149.5	149.3	149.6		149.8	120.9	121.3	121.4	150.3	150.8	150.2	150.2
4′	138.0	137.8	138.1		150.6	140.0	143.2	143.3	151.9	151.9	151.9	151.9
5′	123.5	123.0	123.1		111.0	141.2	145.2	144.0	110.8	110.7	110.7	110.7
6′	131.3	133.1	133.4		129.7	126.8	122.1	122.2	135.9	135.6	136.4	136.1
7′	31.9	31.6	31.7	37.3	123.5	122.8	146.3	147.3	128.4	126.1	128.4	128.5
8′	47.6	44.9	45.1	79.0	129.0	130.1	125.3	125.5	129.2	128.4	130.8	127.1
9′	109.9	110.6	109.6	103.3	66.6	69.3	69.7	69.9	67.4	66.9	67.3	67.6
OCH_3	56.4	55.8	56.2	56.1	55.6		55.9	59.5	55.8	55.8	55.8	55.7
		54.4	56.0		55.2		59.5		56.2	56.2	56.1	56.1
									58.0	58.5	58.7	57.4
									60.1	59.9	60.7	57.8
											61.2	61.3
OCH_2O					101.0	101.1	101.2	101.2	101.2	101.2	101.2	101.2
						101.4						
OC_2H_5			62.7									
			15.3									
$OCOCH_3$	168.8	168.9	169.1									
	20.5	20.6	20.7									
			169.2									
			20.7									

① 化合物 15 在 CD_3COCD_3 中测定；化合物 17～19 在 $(CD_3)_2SO$ 中测定。

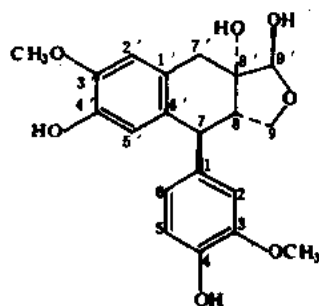


12

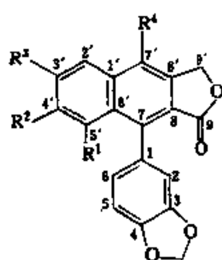


13. R = CH_3

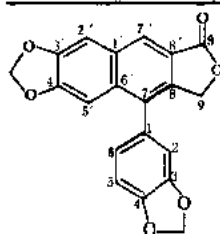
14. R = C_2H_5



15



取代基 / 化合物	R¹	R²	R³	R⁴
16	H	OCH_3	OCH_3	OH
18	OH	OCH_3	H	OCH_3
19	OH	OH	H	OCH_3
20	H	OCH_3	OCH_3	O-$Xyl_{3,4}$ $(OCH_3)_2$
21	H	OCH_3	CH_3	O-Xyl_2 (OAc) -3, 4 $(OCH_3)_2$
22	H	OCH_3	OCH_3	O-Xyl $(OCH_3)_3$
23	H	OCH_3	OCH_3	O-Xyl- $(OCH_3)_3$ (呋喃糖)



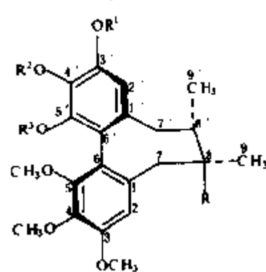
17

第六节 联苯、苯并呋喃及氢化苯并呋喃类木脂素的^{13}C-NMR 化学位移

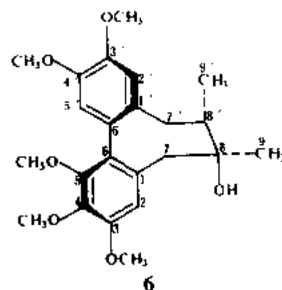
一、联苯类木脂素的^{13}C-NMR 化学位移

表 24-18 联苯类木脂素 1~9 的^{13}C-NMR 化学位移数据

C \ 化合物	1	2	3	4	5	6	7	8	9
1	139.1	139.4	139.1	139.8	140.2	139.3	132.1	131.8	132.5
2	107.3	107.4	107.4	107.3	107.5	107.7	110.4	110.5	110.6
3	153.0	152.9	153.3	153.2	153.2	152.6	152.3	152.3	152.6
4	140.3	139.3	139.9	139.9	139.6	140.1	140.8	140.8	140.8
5	151.6	151.5	151.4	151.3	151.3	151.0	152.1	151.9	152.6
6	122.4	122.3	121.9	131.3	120.9	126.5	124.2	124.2	123.2
7	35.7	35.6	35.6	35.8	35.5	35.7	40.6	40.9	41.1
8	40.9	40.9	40.8	40.9	40.6	40.5	71.7	71.8	72.0
9	21.8	21.8	21.8	21.7	21.6	21.6	30.1	29.7	29.7
1′	133.9	134.7	134.2	134.3	134.0	128.5	132.5	133.8	134.3
2′	110.6	113.1	120.4	107.9	113.1	114.7	105.9	110.1	107.3
3′	151.7	147.6	142.5	150.6	151.5	147.2	147.9	152.0	150.7
4′	139.9	137.7	142.8	134.0	139.4	146.4	135.0	140.0	134.0
5′	151.5	150.4	151.7	146.9	142.3	114.0	143.3	153.6	146.9
6′	123.5	122.6	129.0	117.0	123.5	130.3	121.9	122.8	116.5
7′	33.8	33.8	33.8	33.8	33.8	33.4	33.8	34.4	34.5
8′	39.2	38.8	38.6	39.2	39.2	38.8	42.1	41.8	41.8
9′	12.7	12.6	12.5	12.8	13.0	12.8	15.8	15.9	15.9
OCH_3	55.7	55.9	56.0	55.9	55.9	55.9	56.0	56.0	55.8
	60.3	60.1	60.3	56.0	56.1	56.0	59.6	60.5	56.0
	60.7	60.5	60.6	61.0	56.2	60.5	60.6	60.9	61.0
		61.0	60.8	61.1	60.7	61.1	61.0		61.1
			60.9		60.9				
OCH_2O							100.8		
$OCOCH_3$			169.1		168.4				
			20.8		20.5				



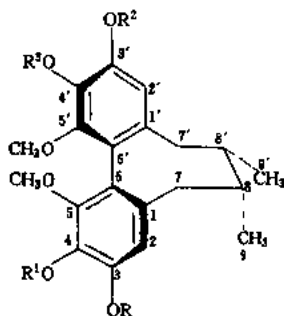
1. $R = H$, $R^1 = R^2 = R^3 = CH_3$
2. $R = R^1 = H$, $R^2 = R^3 = CH_3$
3. $R = H$, $R^1 = Ac$, $R^2 = R^3 = CH_3$
4. $R = R^3 = H$, $R^2 = R^1 = CH_3$
5. $R = H$, $R^1 + R^2 = CH_2$, $R^3 = Ac$
7. $R = H$, $R^3 = Ac$, $R^1 = R^2 = CH_3$
8. $R = OH$, $R^1 + R^2 = CH_2$, $R^3 = CH_3$
9. $R = OH$, $R^1 = R^2 = CH_3$, $R^3 = H$



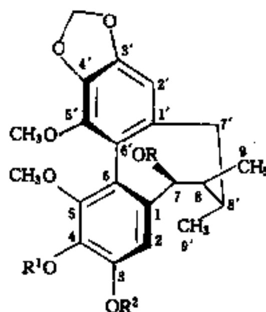
6

表 24-19 联苯类木脂素 10～21 的 ^{13}C-NMR 化学位移数据[55,57～59]

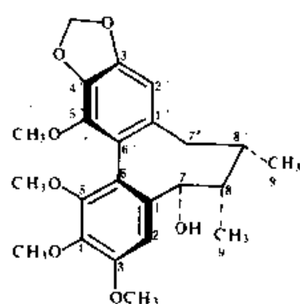
C \ 化合物	10	11	12	13	14	15	16	17	18	19	20	21
1	134.1		134.1	133.9	133.5	134.9	132.8	137.0	136.0	136.5	135.2	130.8
2	110.7		110.8	110.7	110.3	113.3	111.3	110.2	105.6	106.4	105.5	106.5
3	151.6		157.7	152.0	151.3	147.6	151.9	152.1	148.2	152.3	148.1	148.0
4	140.2		140.3	140.3	140.3	137.8	141.7	141.7	136.4	140.8	136.4	137.0
5	151.7		157.6	151.5	151.3	150.3	151.9	151.9	141.6	151.2	141.6	141.7
6	123.4		123.4	122.0	123.3	122.5	123.8	122.2	121.5	121.3	121.6	122.8
7	39.2	38.9	39.6	39.1	39.1	38.9	80.8	81.4	81.1	73.4	81.1	81.2
8	33.6	33.7	33.8	33.7	33.7	33.8	37.0	40.1	40.1	42.8	40.2	36.4
9	12.9	12.6	12.8	12.6	12.7	12.6	15.8	16.6	16.5	7.8	15.6	14.3
1′	137.8		140.0	139.5	138.8	140.2	135.1	135.5	135.7	137.9	137.2	136.9
2′	102.9		110.0	117.5	107.0	110.2	102.2	102.5	102.7	102.8	107.1	107.1
3′	148.7		148.8	143.7	152.7	148.8	148.8	149.2	149.3	149.2	153.6	153.2
4′	134.6		137.5	142.4	139.6	137.5	134.6	134.6	134.5	134.6	140.1	140.1
5′	141.1		150.3	151.6	151.5	150.5	142.0	141.5	141.6	140.9	151.9	151.8
6′	121.4		121.6	128.0	122.2	121.5	121.7	120.7	120.4	119.6	121.3	122.8
7′	35.6	35.4	35.3	35.1	35.5	35.3	37.9	38.1	37.9	34.7	37.3	37.9
8′	40.8	40.8	40.9	40.9	40.7	41.0	37.2	37.2	37.1	39.3	36.6	37.2
9′	21.5	21.7	21.7	21.7	21.8	21.7	17.8	17.5	17.5	22.0	18.7	19.2
OCH_3	55.9	59.6	56.0	56.6	55.7	61.0	56.0	56.0	59.5	56.0	55.9	56.0
	59.6		60.1	60.3	60.4	60.1	59.3	59.5	59.6	59.6	59.6	59.7
	60.5		60.5	60.6	60.8		60.4	60.3		60.6	60.7	60.2
	61.0		60.9	60.8			60.9	60.8		61.0	60.9	60.7
			61.0	61.0								
OCH_2O	100.7						100.7	100.7	100.8		101.7	101.3
									101.2			
$OCOCH_3$				169.0								
				20.8								



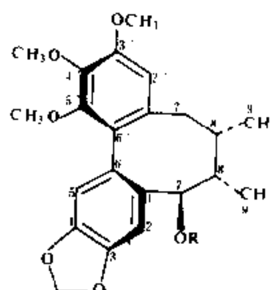
10. $R = R^1 = CH_3$, $R^2 + R^3 = CH_2$
11. $R + R^1 = R^2 + R^3 = CH_2$
12. $R = R^1 = R^3 = CH_3$, $R^2 = H$
13. $R = R^1 = R^3 = CH_3$, $R^2 = Ac$
14. $R = R^1 = R^2 = R^3 = CH_3$
15. $R = R^3 = CH_3$, $R^2 = R^1 = H$



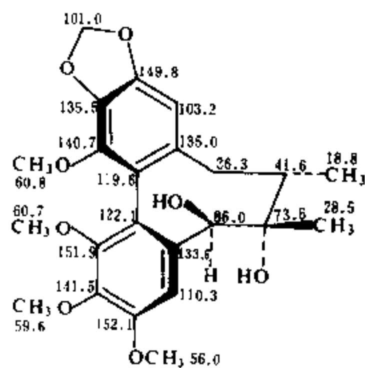
16. R = CO, $R^1 = R^2 = CH_3$
17. $R = H$, $R^1 = R^2 = CH_3$
18. $R = H$, $R^1 + R^2 = CH_2$



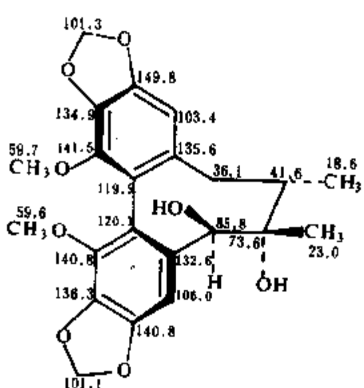
19



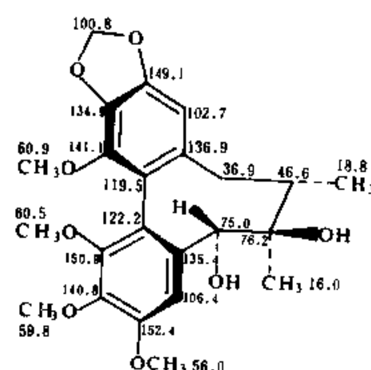
20. R = H
21. R = C_6H_5CO



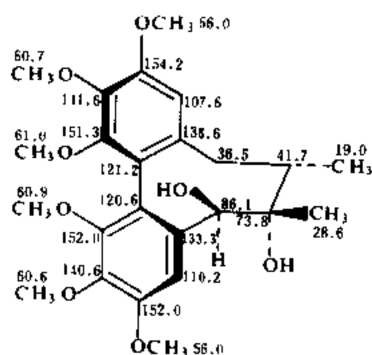
22[55]



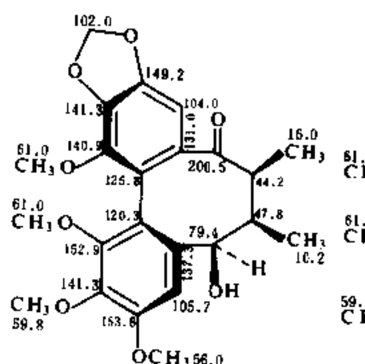
23[58]



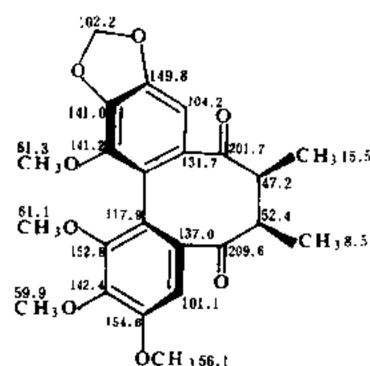
24[55]



25[58]



26[60]



27[60]

二、苯并呋喃类木脂素的^{13}C-NMR 化学位移

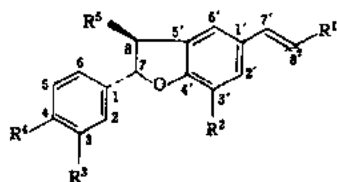
表 24-20 苯并呋喃类木脂素 1～14 的^{13}C-NMR 化学位移数据[12,22,47～50]

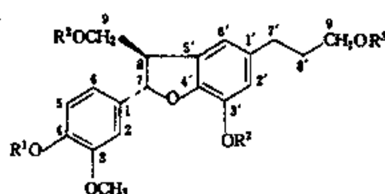
C \ 化合物	1	2	3①	4①	5①	6	7	8	9①	10	11	12	13	14
1	131.6	134.0	133.8	134.3	134.6	132.5	139.6	139.5	137.9	137.4	137.3	137.5	129.1	130.2
2	108.6	106.3	128.1	110.7	110.5	109.8	109.4	109.8	111.5	109.8	110.2	110.9	108.6	113.1
3	146.1	147.5	116.2	148.6	148.2	148.3	151.1	150.9	146.8	150.7	150.7	150.4	146.5	145.2
4	146.3	147.2	158.1	147.3	147.0	146.9	139.2	139.3	150.1	145.5	145.8	147.1	145.6	145.2
5	113.8	107.7	116.2	115.8	116.3	115.5	122.7	122.6	116.8	120.1	120.1	117.5	114.3	115.3
6	119.3	119.7	128.1	119.5	119.5	119.4	117.3	118.0	118.9	117.4	118.5	119.5	119.1	116.6
7	93.3	93.0	88.3	88.3	88.1	87.0	87.8	87.6	87.6	87.8	87.8	88.4	88.8	87.5
8	45.2	45.5	54.6	54.6	55.1	55.9	51.1	50.7	56.5	51.1	50.7	54.7	52.9	52.9

续表

C \ 化合物	1	2	3①	4①	5①	6	7	8	9①	10	11	12	13	14
9	17.2	17.6	64.5	64.5	64.7	68.2	65.5	65.4	64.6	65.5	65.4	64.5	63.7	63.0
1′	131.7	131.8	129.4	130.4	129.7	128.9	127.8	126.8	129.1	127.9	126.8	129.7	127.8	127.4
2′	112.9	113.0	123.7	111.8	115.7	114.6	122.2	112.5	117.2	121.9	112.4	111.7	112.3	117.0
3′	132.8	132.7	109.8	145.1	141.5	143.8	134.7	143.9	141.2	134.7	143.9	145.0	144.4	141.3
4′	146.6	146.2	160.5	148.9	146.0	145.1	148.7	145.9	145.9	148.8	145.9	148.7	151.2	150.2
5′	143.6	143.7	129.9	132.0	136.2	137.9	133.6	134.9	136.5	133.6	134.9	132.2	132.0	132.3
6′	109.0	109.2	128.1	116.2	116.9	114.8	121.9	16.1	116.8	122.3	116.1	116.1	118.0	116.6
7′	130.5	130.6	130.9	130.9	35.6	34.9	31.5	32.0	35.1	31.5	32.1	131.6	152.9	125.5
8′	122.8	122.9	128.0	128.0	31.9	30.9	30.3	30.5	32.2	30.3	30.6	127.3	126.0	154.0
9′	18.0	18.1	63.3	63.3	61.9	68.2	63.6	63.1	62.1	63.6	63.7	63.5	193.2	193.8
OCH_3	55.5	55.7			56.3	55.9	55.9	55.8	56.5	56.1	55.1	56.4	55.9	
								56.0			56.0		56.0	
OCH_2O		100.7												
$OCOCH_3$							168.1	168.6		168.2				
							168.7	170.4		169.1				
							170.8	170.8		169.9				
							170.8	20.6		170.3				
							20.7	20.8		170.4				
							20.8	20.9		170.9				
							20.9			20.7				
										20.9				
										21.0				

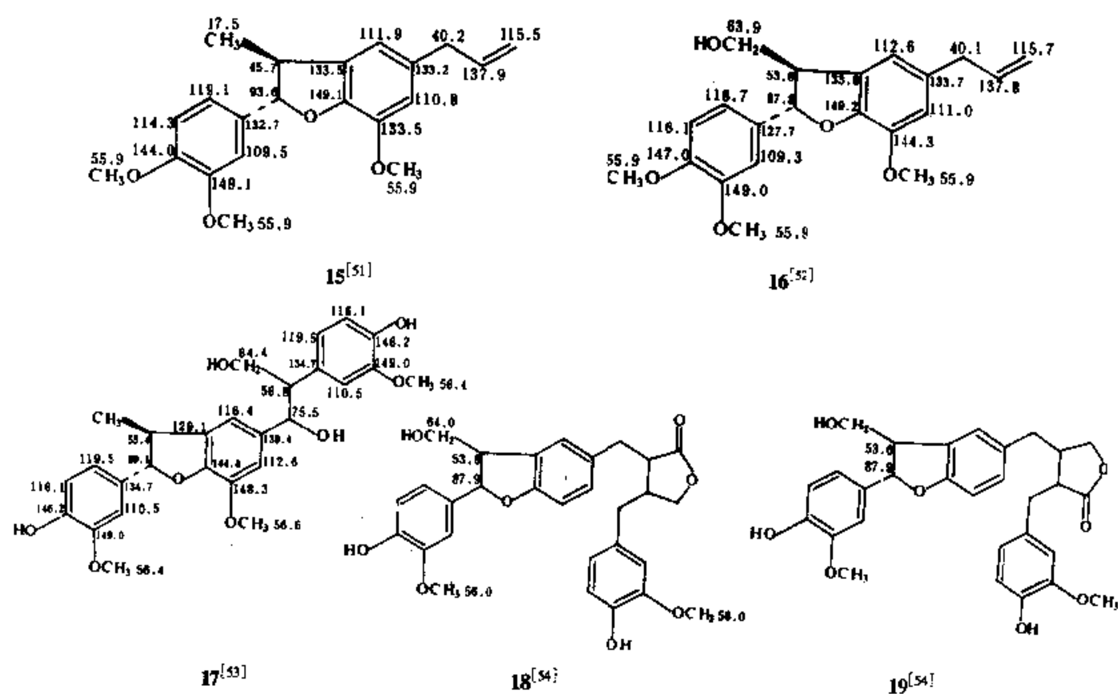
① 化合物3~4在$D_2O+CD_3COCD_3$中测定；化合物5在CD_3COCD_3中测定；化合物9在CD_3OD中测定。





化合物 \ 取代基	R¹	R²	R³	R⁴	R⁵
1	CH_3	OCH_3	OCH_3	OH	CH_3
2	CH_3	OCH_3	OCH_2O		CH_3
3	CH_2OH	H	OCH_3	OH	CH_2OH
4	CH_2OH	OCH_3	OCH_3	OH	CH_2OH
12	CH_2OH	OCH_3	OCH_3	OGlu	CH_2OH
13	CHO	OCH_3	OCH_3	OH	CH_2OH
14	CHO	OH	OH	OH	CH_2OH

化合物 \ 取代基	R¹	R²	R³
5	H	H	H
6	H	CH_3	H
7	$COCH_3$	$COCH_3$	$COCH_3$
8	$COCH_3$	CH_3	$COCH_3$
9	Glu	H	H
10	Glu (OAc)$_4$	$COCH_3$	$COCH_3$
11	Glu (OAc)$_4$	CH_3	$COCH_3$



15[51]　16[52]　17[53]　18[54]　19[54]

三、氢化苯并呋喃类木脂素的^{13}C-NMR化学位移

表 24-21　氢化苯并呋喃类木脂素 1～10 的^{13}C-NMR 化学位移数据[12,62]

C \ 化合物	1	2	3	4	5	6	7	8	9	10
1	135.5	132.7	133.9	131.5	129.8	130.1	130.2	134.6	130.7	129.8
2	102.6	103.5	100.2	106.5	109.1	109.2	106.0	99.7	102.4	106.2
3	152.8	153.3	148.6	148.1	149.6	149.5	147.7	148.9	153.2	147.8
4	137.2	138.4	133.9	148.1	149.2	149.2	147.1	131.0	132.1	147.8
5	152.8	153.3	143.1	107.8	110.9	110.9	108.1	143.4	153.2	108.2
6	102.6	103.5	105.5	120.5	119.3	119.2	118.7	105.0	102.4	118.7
7	94.3	91.2	81.8	90.9	91.0	91.5	87.2	87.1	87.2	87.4
8	46.9	49.8	44.8	49.5	49.3	49.6	44.6	44.5	44.5	42.8
9	16.1	6.9	10.8	8.3	8.5	8.5	12.0	11.9	12.0	11.6
1′	142.5	142.8	52.5	153.3	153.3	152.7	152.7	152.6	152.6	48.7
2′	131.6	130.9	99.7	107.8	107.8	107.2	109.0	108.9	108.9	167.0
3′	80.9	77.6	192.6	50.9	51.0	49.8	53.9	53.8	53.9	166.6
4′	172.6	174.3	125.7	181.4	181.3	183.9	181.2	181.0	181.1	192.3
5′	104.6	102.7	150.9	101.8	101.9	166.0	101.8	101.8	102.0	77.3
6′	186.8	186.8	31.0	182.8	182.6	189.7	182.4	182.3	182.4	32.2
7′	33.2	33.5	40.4	36.6	36.7	36.7	43.9	43.8	43.9	39.8
8′	134.8	134.8	133.9	130.9	130.7	130.7	131.5	131.5	131.5	132.7
9′	116.9	117.1	111.6	120.0	119.9	119.8	120.0	120.0	120.1	119.8
OCH_3	56.1	56.1	56.4	51.8	55.2	55.3	55.2	56.7	56.1	55.9
	60.7	60.7			55.9	55.9		55.1	60.7	
	50.3	51.1				60.4			55.2	
OCH_2O			101.2	101.2			101.0	101.4		101.1

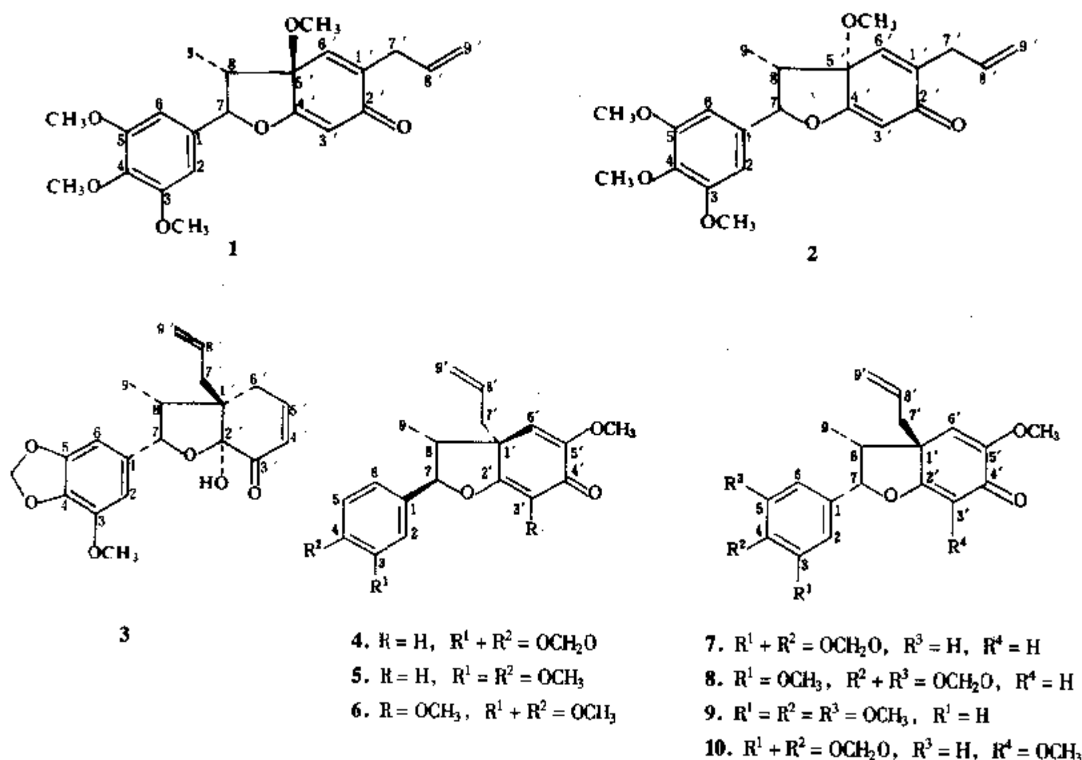
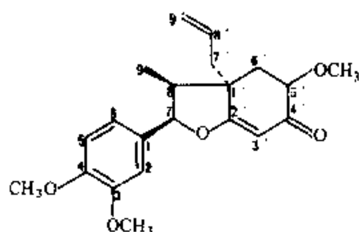
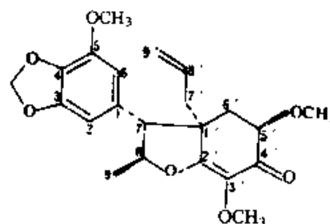


表 24-22 氢化苯并呋喃类木脂素 11 ~ 16 的 ^{13}C-NMR 化学位移数据[12,63-65]

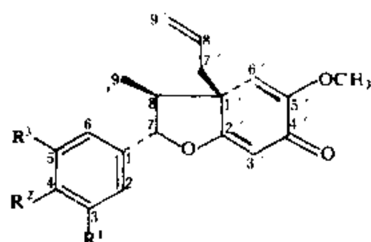
C \ 化合物	11	12	13	14	15	16	C \ 化合物	11	12	13	14	15	16
1	128.3	129.9	133.1	136.1	131.4	133.2	3′	50.2	101.9	101.9	127.4	140.2	140.0
2	108.6	109.2	103.4	102.3	106.1	103.0	4′	183.4	182.7	182.7	192.7	172.0	171.0
3	148.8	149.6	153.3	149.7	148.1	153.4	5′	100.1	153.0	153.0	77.2	99.5	99.6
4	148.5	149.2	131.5	130.2	148.1	138.5	6′	196.6	107.9	107.9	37.8	199.3	199.2
5	110.9	110.9	153.5	143.4	108.2	153.4	7′	39.0	36.7	36.7	39.1	45.0	44.8
6	117.8	119.4	103.4	109.1	120.0	103.0	8′	131.5	130.8	130.8	133.7	130.7	130.8
7	87.2	91.1	91.1	62.1	93.7	93.7	9′	119.7	119.9	119.9	118.8	119.0	118.8
8	42.5	49.4	49.4	82.2	42.6	42.6	OCH_3	55.9	55.9	56.1	57.1	53.5	56.1
9	11.6	8.5	8.5	18.9	16.1	16.3		58.7	55.2	60.7	59.3		60.7
1′	76.8	51.0	51.0	48.3	80.8	80.6					60.3		53.4
2′	32.0	181.4	181.4	169.6	134.1	134.1	OCH_2O				101.7	100.3	

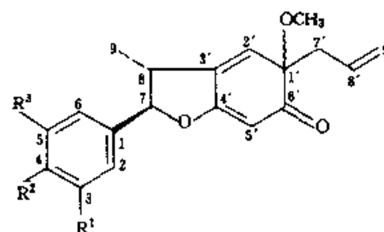


11



14





12. $R^1 = R^2 = OCH_3$，$R^3 = H$　　**15.** $R^1 + R^2 = OCH_2O$，$R^3 = H$

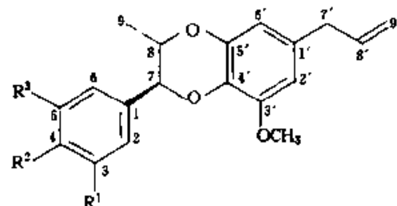
13. $R^1 = R^2 = R^3 = OCH_3$　　**16.** $R^1 = R^2 = R^3 = OCH_3$

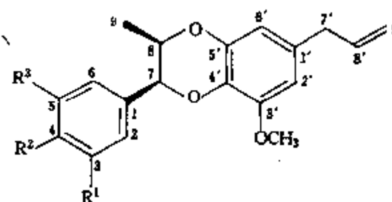
第七节　苯并二氧六环及双环辛烷类木脂素的13C-NMR化学位移

一、苯并二氧六环类木脂素的13C-NMR的化学位移

表 24-23　苯并二氧六环类木脂素 1～7 的13C-NMR化学位移数据[50,61,66,67]

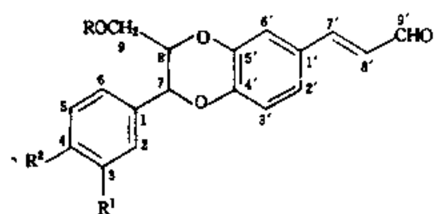
C \ 化合物	1	2	3	4	5	6	7
1	132.4	130.7	129.6	129.5	127.2	134.2	129.4
2	104.4	107.1	103.2	111.2	115.0	123.0	116.1
3	153.4	147.9	153.5	149.1	145.3	142.5	143.2
4	138.3	147.9	137.8	148.9	145.9	142.1	144.0
5	153.4	108.2	153.5	109.5	115.5	123.9	116.7
6	104.4	121.3	103.2	118.7	118.9	126.0	120.4
7	81.0	80.6	77.1	77.1	76.1	75.4	75.2
8	74.0	74.1	73.2	73.2	78.1	74.3	78.2
9	17.3	17.2	12.6	12.7	60.1	62.0	60.0
1′	132.2	132.2	132.5	132.5	127.6	128.1	127.5
2′	104.5	104.5	105.1	104.9	122.6	123.0	116.7
3′	148.4	148.4	148.1	149.2	117.3	117.5	143.7
4′	131.1	131.1	132.3	132.3	146.5	145.8	146.1
5′	143.8	144.2	143.4	143.5	143.5	142.7	117.3
6′	109.4	109.4	109.8	109.8	116.8	116.9	123.0
7′	39.9	40.0	40.0	40.1	126.8	127.2	126.9
8′	137.1	137.2	137.5	137.5	153.0	152.6	152.9
9′	115.6	115.6	115.9	115.9	194.0	193.9	193.9
OCH_3	56.3	56.1	56.2	56.0			
	60.7		60.9	56.1			
			56.1				
OCH_2O		101.1					
$OCOCH_3$						168.0	
						20.2	
						169.8	
						20.2	



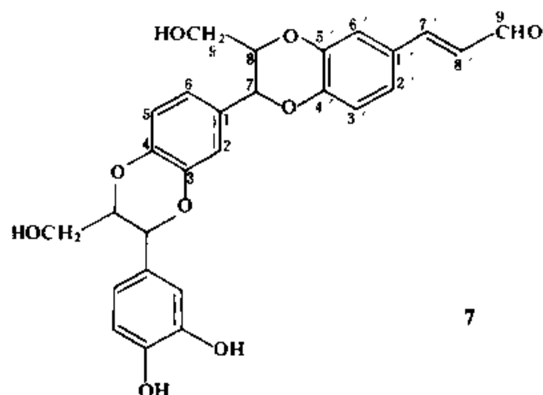


1. $R^1 = R^2 = R^3 = OCH_3$　　**3.** $R^1 = R^2 = R^3 = OCH_3$

2. $R^1 + R^2 = OCH_2O$，$R^3 = H$　　**4.** $R^1 = R^2 = OCH_3$，$R^3 = H$



5. R = H, $R^1 = R^2 = OH$
6. R = Ac, $R^1 = R^2 = OAc$

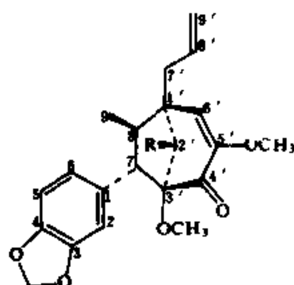


7

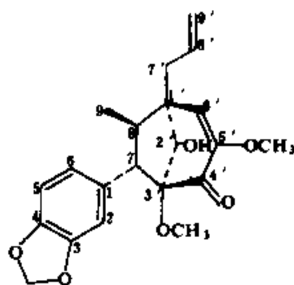
二、双环辛烷类木脂素的^{13}C-NMR化学位移

表 24-24 双环辛烷类木脂素 1～7 的^{13}C-NMR 化学位移数据[63,64,68]

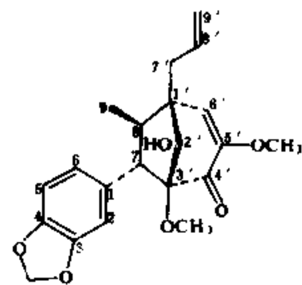
C \ 化合物	1	2	3	4	5	6	7
1	131.4	131.0	132.2	133.3	137.2	140.3	136.7
2	107.6	107.7	107.9	108.2	104.6	104.7	140.5
3	147.4	147.5	147.5	148.0	153.8	153.7	153.9
4	146.3	146.5	146.4	147.8	137.2		136.7
5	110.8	110.6	109.6	108.7	153.8	153.7	153.9
6	120.3	119.5	119.4	121.4	104.6	104.7	104.5
7	57.0	57.5	55.6	53.1	45.4	45.4	45.3
8	48.6	49.4	46.3	47.4	49.5	46.0	46.6
9	13.9	13.9	13.4	17.4	13.9	11.9	15.6
1′	51.4	50.8	48.1	51.8	140.6	140.3	140.1
2′	78.2	77.6	84.5	80.9	202.2	76.3	189.3
3′	90.8	90.2	90.2	64.9	69.9	58.9	66.4
4′	194.6	193.6	195.8	185.8	194.2		
5′	151.4	152.1	151.2	153.0	89.4	85.5	94.5
6′	123.8	124.1	123.0	126.8	147.3	126.6	143.6
7′	36.6	37.1	38.1	36.4	32.8	36.4	34.1
8′	134.4	133.9	132.4	134.3	134.1	135.1	133.8
9′	117.9	118.6	117.9	118.2	118.0	117.3	118.5
OCH_3	54.5	54.8	53.5	55.3	54.0	56.3	56.3
	55.4	55.5	55.4		56.3	60.8	60.9
					60.8	52.9	51.0
OCH_2O	100.8	100.9	100.8	100.9			
$OCOCH_3$		169.1					
		21.0					



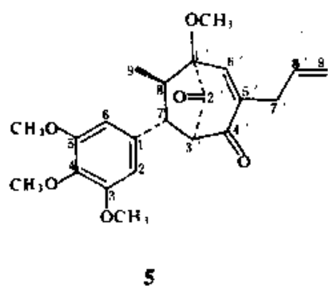
1. R = OH
2. R = OAc



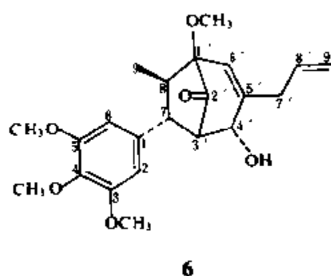
3



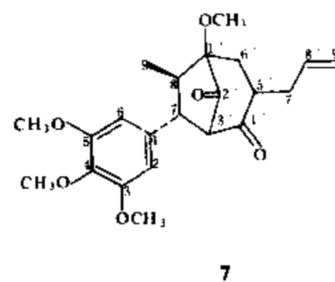
4



5



6

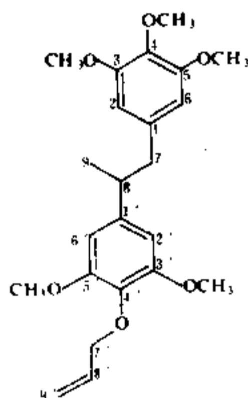


7

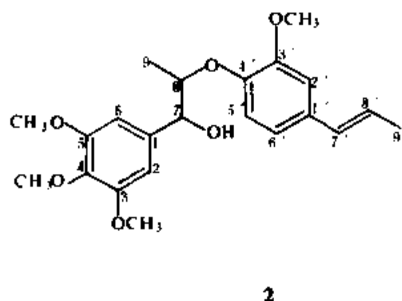
第八节　其他类型木脂素的^{13}C-NMR 化学位移

表 24-25　其他类型木脂素 1～7 的^{13}C-NMR 化学位移数据[12,64,69,70]

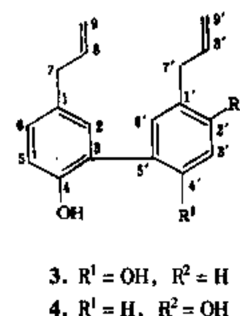
C \ 化合物	1	2	3	4	5	6	7
1	135.8	137.6	133.3	132.4	133.3	50.3	50.4
2	105.7	104.2	131.4	131.1	129.8	180.1	180.1
3	152.6	152.9	124.5	127.8	117.8	101.4	101.4
4	135.6	135.5	151.0	150.7	155.2	183.1	183.1
5	152.6	152.9	116.8	116.8	117.8	153.4	153.3
6	105.7	104.2	129.8	129.6	129.8	109.0	109.0
7	45.2	83.6	39.4	39.4	39.5	43.7	43.6
8	41.9	78.0	137.6	137.8	137.4	81.9	81.9
9	20.8	17.0	115.8	115.6	115.8	38.0	37.9
1′	141.9	133.3	133.3	126.5	132.5	137.3	139.1
2′	103.8	109.1	131.4	153.9	111.1	107.7	104.8
3′	152.2	150.5	124.5	116.5	144.0	148.0	153.3
4′	134.5	146.4	151.0	130.3	135.0	146.4	139.1
5′	152.2	118.6	116.8	128.6	144.9	108.3	153.3
6′	103.8	118.7	129.8	128.8	111.5	121.1	104.8
7′	73.7	130.2	39.4	35.0	39.4	46.2	46.9
8′	134.2	124.6	137.6	136.1	137.2	45.5	45.3
9′	116.9	18.2	115.8	115.6	115.7	14.5	14.6
OCH_3	55.6	55.6				55.2	55.2
	55.7	56.0					56.2
	60.4	60.7					60.8
OCH_2O						101.0	



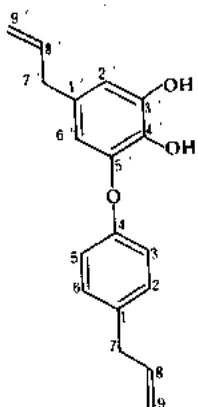
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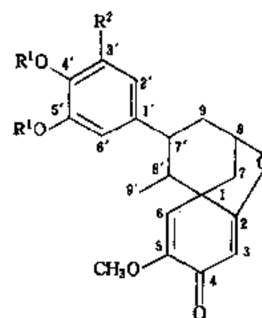
2



3. R^1 = OH，R^2 = H
4. R^1 = H，R^2 = OH

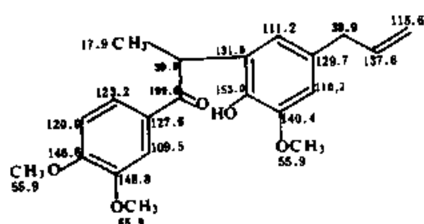


5

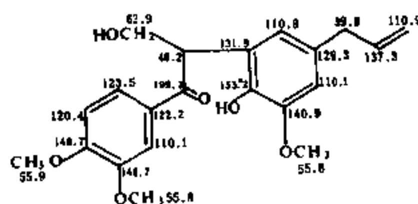


6. $R^1 + R^1 = CH_2$, $R^2 = H$

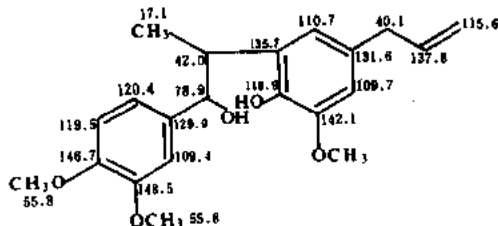
7. $R^1 = CH_3$, $R^2 = OCH_3$



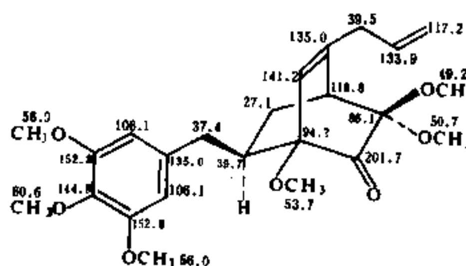
8[51]



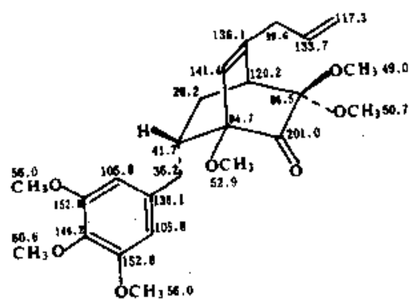
9[52]



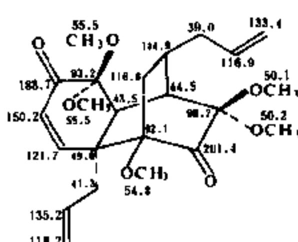
10[51]



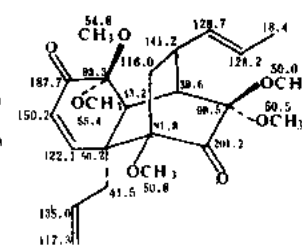
11[71]



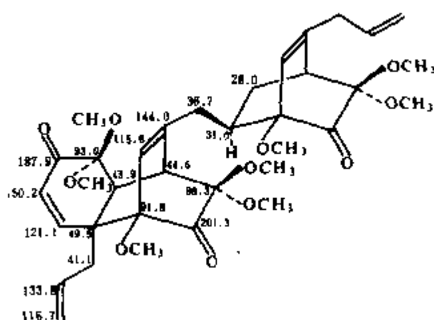
12[71]



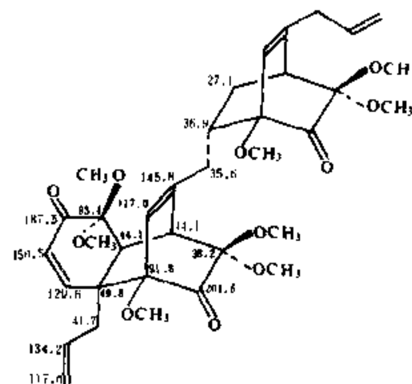
13[71]



14[71]



15[71]



16[71]

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第二十五章　甾族化合物的^{13}C-NMR 化学位移

甾体化合物的^{13}C-NMR 图谱中，各碳原子的峰很少重叠，可以提供结构的信息很多，使该类化合物的结构测定更加方便。

1. 一般甾体化合物中^{13}C-NMR 的各种碳化学位移范围

伯烷碳大约 $\delta = 12 \sim 24$，仲烷碳 $\delta = 20 \sim 41$，叔烷碳 $\delta = 35 \sim 57$，季碳 $\delta = 27 \sim 43$，与羟基连接的碳 $\delta = 65 \sim 91$，不饱和碳 $\delta = 119 \sim 172$，羰基碳 $\delta = 177 \sim 220$。

2. 胆甾烷衍生物的^{13}C-NMR 化学位移的特征

① 对于其侧链，如果无羟基取代，几乎为一定值。

② 在 C-3 位引入羰基时，C-3 的化学位移大幅度移向低场，C-2 和 C-4 的化学位移也移向低场（β-效应）。

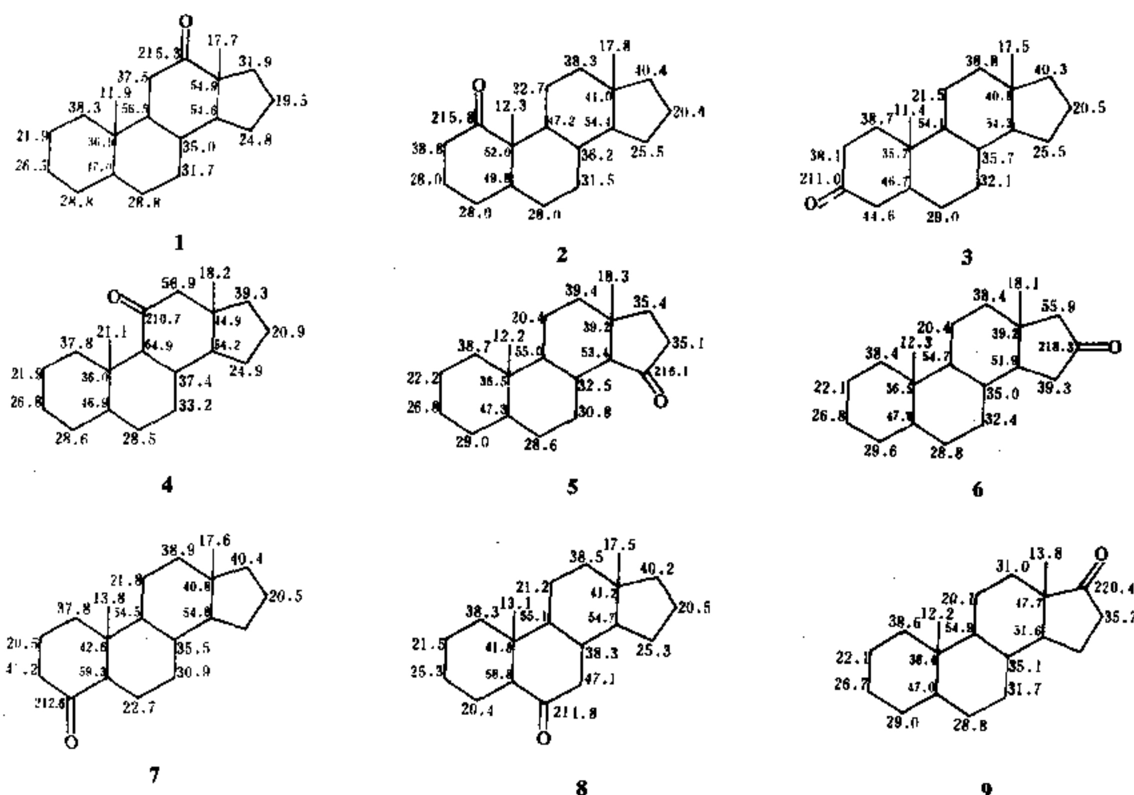
③ 由于 γ-效应的影响，亚甲基 C-11 受到两个角甲基的 γ-效应，而 C-15 受到一个角甲基的 γ-效应的影响，所以 C-11 的化学位移比 C-15 的化学位移处于高场。

④ 如果羟基被乙酰化，α 碳向低场位移 3～4 个单位，β 碳向高场位移 2～3 个化学位移单位，α-羟基乙酰化物比 β-羟基乙酰化物的 C-5 化学位移明显向高场位移。

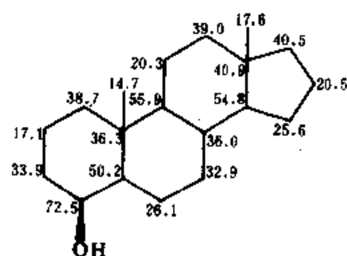
⑤ 5β-甾体化合物的 C-19 化学位移比 5α-甾体化合物的化学位移低 11～12 个化学位移单位。

第一节　雄甾烷类化合物的^{13}C-NMR 化学位移

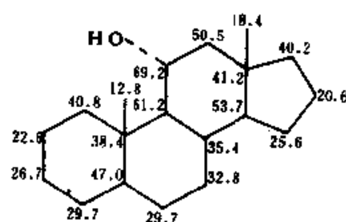
一、雄甾酮类化合物的^{13}C-NMR 化学位移[1]



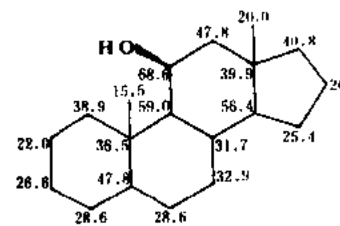
二、雄甾醇类化合物的^{13}C-NMR化学位移[2]



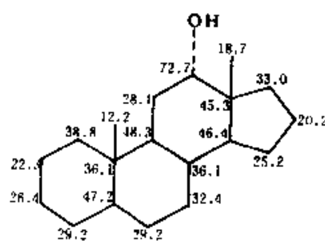
10



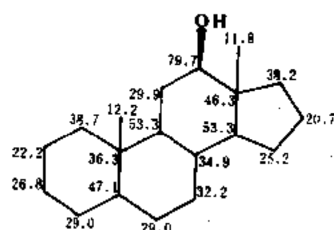
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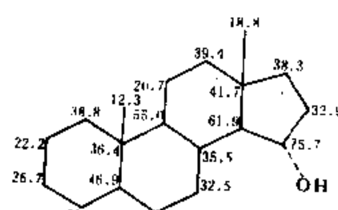
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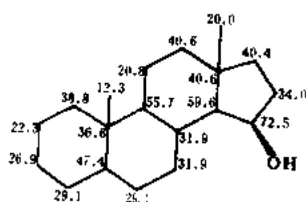
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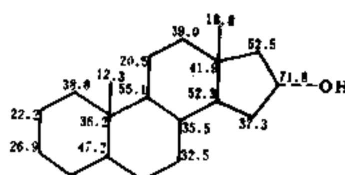
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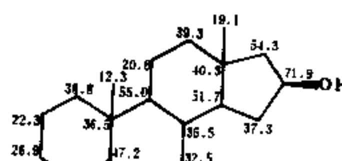
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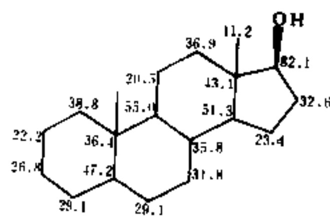
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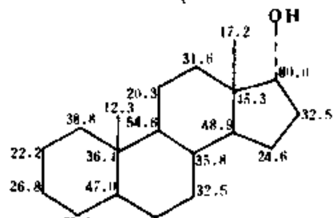
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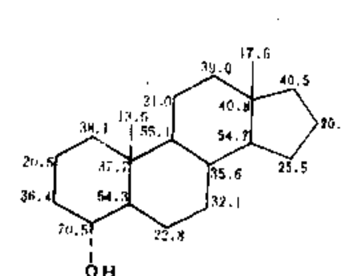
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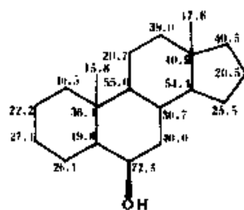
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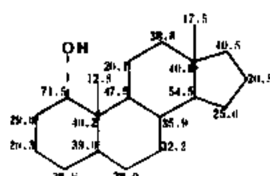
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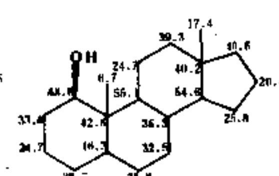
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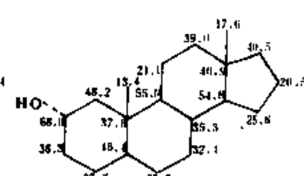
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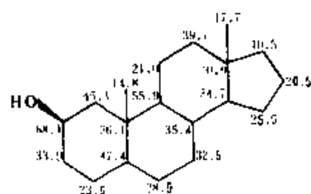
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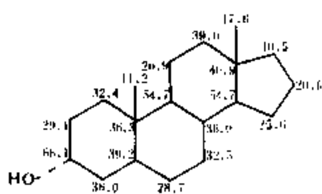
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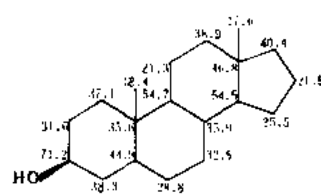
25



26



27

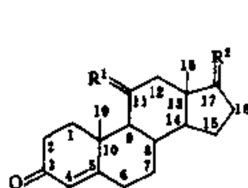


28

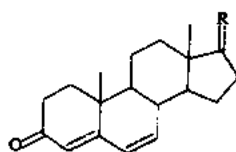
三、雄甾烯酮类化合物的¹³C-NMR 化学位移

表 25-1 雄甾烯酮类化合物 29～41 的¹³C-NMR 化学位移数据[6]

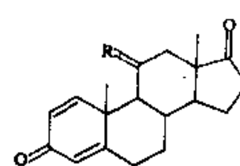
C \ 化合物	29	30	31	32	33	34	35	36	37	38	39	40	41
1	35.5	35.6	33.9	33.9	155.2	34.6	154.8	39.0	39.3	37.7	32.9	32.8	49.2
2	33.7	33.8	33.9	33.9	127.6	33.6	127.6	24.0	23.4	27.2	23.4	23.4	197.7
3	198.9	199.4	199.2	199.1	186.0	199.2	185.9	26.8	26.8	71.9	136.6	136.9	143.6
4	123.9	123.6	124.1	123.7	124.0	124.6	124.7	32.7	32.8	35.7	127.7	127.6	131.3
5	170.1	171.0	162.9	163.2	168.2	167.8	165.9	169.2	168.9	164.2	161.1	161.3	157.2
6	32.3	32.7	128.7	128.1	32.3	31.9	32.1	124.3	124.4	126.3	124.1	123.9	129.5
7	31.1	31.5	138.3	139.9	31.2	30.8	31.9	200.8	201.4	200.8	202.0	201.5	200.7
8	34.9	35.0	37.0	37.3	35.0	36.2	35.9	44.3	45.0	44.9	46.4	45.5	45.0
9	53.6	53.9	48.7	48.0	52.3	63.2	60.6	45.7	45.0	44.9	48.8	45.5	45.3
10	38.4	38.6	36.1	36.5	43.4	38.2	42.3	39.2	39.3	38.3	36.3	36.3	39.7
11	20.1	20.6	20.0	20.1	22.0	207.4	207.4	20.1	20.4	20.6	20.7	20.7	20.6
12	30.5	36.4	31.3	36.0	32.5	50.3	50.3	30.7	35.9	35.9	39.7	36.0	35.6
13	47.3	42.7	48.3	43.4	47.6	50.3	50.0	47.8	43.1	43.0	41.7	43.4	43.4
14	50.6	50.4	50.7	50.6	50.4	49.6	49.1	50.4	50.2	49.7	49.9	49.6	49.2
15	21.5	23.2	21.4	23.1	21.8	21.5	21.6	21.8	26.0	25.8	27.7	26.0	25.7
16	35.5	30.1	35.6	27.4	35.5	35.9	35.9	35.5	27.6	27.4	21.2	27.6	27.5
17	220.0	81.0	219.3	82.0	219.6	219.7	216.4	220.0	82.0	81.7	38.0	82.0	81.7
18	13.5	11.0	13.7	12.0	13.8	14.6	14.6	13.7	12.1	12.0	17.4	12.1	12.1
19	17.2	17.3	16.3	16.3	18.7	17.2	18.9	17.4	17.4	17.2	16.6	16.6	19.5



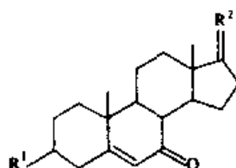
29. $R^1 = H_2$, $R^2 = O$
30. $R^1 = H_2$, $R^2 = \alpha-H$, $\beta-OH$
34. $R^1 = R^2 = O$



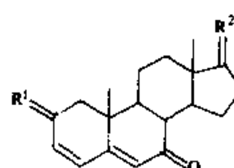
31. $R = O$
32. $R = \alpha-H$, $\beta-OAc$



33. $R = H_2$
35. $R = O$



36. $R^1 = H$, $R^2 = O$
37. $R^1 = H$, $R^2 = \alpha-H$, $\beta-OAc$
38. $R^1 = OAc$, $R^2 = \alpha-H$, $\beta-OAc$

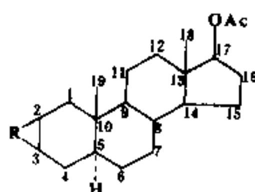


39. $R^1 = R^2 = H_2$
40. $R^1 = H$, $R^2 = \alpha-H$, $\beta-OAc$
41. $R^1 = O$, $R^2 = \alpha-H$, $\beta-OAc$

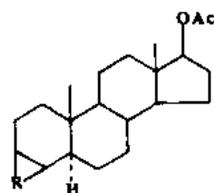
四、带氧环和硫环雄甾烷类化合物的^{13}C-NMR化学位移

表 25-2　带氧环和硫环雄甾烷类化合物 42～59 的^{13}C-NMR化学位移数据

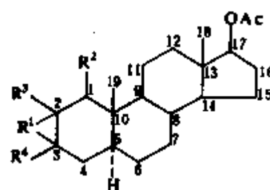
C \ 化合物	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59
1	38.2	38.1	40.3	39.3	30.4	33.6	30.4	35.0	34.0	43.4	38.8	35.4	43.7	39.1	40.1	46.5	41.2	47.1
2	50.4	52.6	34.6	36.8	21.3	21.2	23.5	22.5	58.6	57.7	60.1	55.9	56.4	58.3	45.7	47.3	44.3	46.7
3	51.7	51.5	37.6	35.2	51.9	50.3	36.2	33.5	50.4	58.9	57.2	53.1	59.4	57.2	46.7	44.5	48.5	46.7
4	29.0	28.4	30.5	30.1	55.6	57.6	40.5	43.0	28.7	29.3	33.7	29.9	29.7	34.2	37.5	31.1	37.4	31.5
5	36.2	41.2	35.4	43.0	46.7	46.2	50.7	46.4	35.8	41.8	41.7	30.8	35.9	37.3	43.2	43.1	37.0	35.3
6	28.2	28.2	28.1	28.3	26.7	25.3	28.3	27.5	28.4	28.1	28.2	28.5	28.1	28.2	28.3	28.2	28.0	27.9
7	31.1	31.3	31.0	31.3	31.4	31.8	31.4	31.8	31.0	31.4	31.3	30.8	31.2	31.1	31.3	31.3	31.0	31.1
8	35.4	34.7	35.0	34.6	35.3	35.4	35.3	35.3	34.6	34.8	34.8	35.4	35.5	35.4	34.6	34.8	35.3	34.8
9	53.5	65.3	53.6	56.1	52.6	54.7	52.6	55.2	49.1	55.6	55.3	48.5	53.6	53.5	56.1	56.4	53.5	53.3
10	33.6	34.3	35.2	34.6	34.6	35.7	36.2	35.7	36.1	34.8	33.7	36.1	34.1	33.9	34.1	34.8	35.3	35.7
11	20.5	20.5	20.2	20.3	20.5	20.5	20.8	19.9	20.5	20.5	20.5	20.5	20.5	20.5	20.4	20.2	20.3	20.2
12	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9
13	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5	42.5
14	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8	50.8
15	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5	23.5
16	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6	27.6
17	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7	82.7
18	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
19	12.9	14.0	12.6	14.8	13.4	14.0	12.9	14.4	15.7	13.4	13.8	14.5	12.6	13.0	14.4	13.9	12.6	12.0



42. R＝2α，3-O
43. R＝2β，3-O
44. R＝2α，3-S
45. R＝2β，3-S



46. R＝3α，4-O
47. R＝3β，4-O
48. R＝3α，4-S
49. R＝3α，4-S

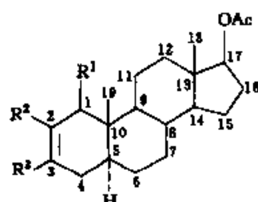


化合物 \ 取代基	R^1	R^2	R^3	R^4
50	2β，3-O	α-CH_3	H	H
51	2β，3-O	H	CH_3	H
52	2β，3-O	H	H	CH_3
53	2α，3-O	α-CH_3	H	H
54	2α，3-O	H	CH_3	H
55	2α，3-O	H	H	CH_3
56	2β，3-S	H	H	CH_3
57	2β，3-S	H	CH_3	H
58	2α，3-S	H	H	CH_3
59	2α，3-S	H	CH_3	H

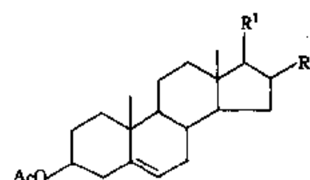
五、雄甾烯醇类化合物的13C-NMR化学位移

表 25-3　雄甾烯醇类化合物 60～70 的13C-NMR 化学位移数据[11,12]

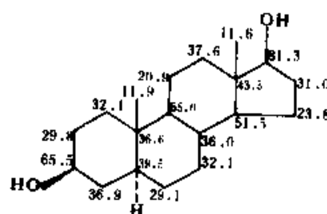
C \ 化合物	60	61	62	63	64	65	66	67	68	69	70
1	38.6	45.0	40.1	36.8	37.0	37.0	36.9	36.9	36.9	37.0	36.9
2	132.8	132.4	119.7	27.6	27.7	27.7	27.7	27.8	27.6	27.7	27.7
3	123.8	119.6	132.3	73.7	73.8	73.8	73.7	73.8	73.8	73.8	73.7
4	31.1	30.5	35.2	37.9	38.1	38.1	38.1	38.1	38.0	38.1	38.1
5	34.6	41.4	41.9	139.5	139.7	139.5	139.7	139.7	139.7	139.6	139.6
6	28.8	28.5	28.5	122.1	122.1	122.3	122.0	121.9	121.7	121.1	121.1
7	31.1	31.5	31.5	31.7	31.7	32.0	31.5	31.5	30.9	32.0	31.8
8	35.5	35.5	35.4	31.3	31.5	31.6	31.1	31.4	31.5	31.5	31.3
9	47.9	54.2	54.0	50.0	49.9	49.8	49.8	49.9	49.7	49.6	49.6
10	36.9	35.0	34.4	36.5	36.6	36.5	36.6	36.6	36.9	36.6	36.6
11	20.5	20.5	20.5	20.5	20.5	20.4	20.4	20.4	20.2	20.3	20.1
12	36.9	36.9	36.9	36.6	36.6	32.0	30.0	37.3	37.3	32.0	31.8
13	42.5	42.5	42.5	42.4	42.4	44.5	43.1	43.7	44.3	44.2	45.5
14	50.8	50.8	50.8	51.1	51.0	50.2	49.9	49.9	48.7	51.2	49.2
15	23.5	23.5	23.5	23.2	23.6	24.8	27.8	32.9	32.9	29.7	28.5
16	27.8	27.8	27.8	30.1	27.5	30.5	40.2	45.8	45.8	45.6	38.4
17	82.7	82.7	82.7	81.4	82.7	81.7	83.8	83.8	83.8	83.4	80.5
18	12.0	12.0	12.0	10.9	11.9	16.4	12.8	12.6	12.7	16.8	16.4
19	13.8	11.8	12.0	19.2	19.3	19.3	19.3	19.3	19.3	19.3	19.3
CH_3CO	21.0	21.0	21.0	21.3	21.4	21.2			21.3	21.4	21.4
CH_3CO	170.6	170.6	170.6	170.4	170.4	170.4			170.8	170.9	170.9
CH_3	15.7	24.1	23.0						65.2	66.6	64.0



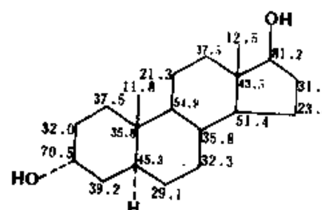
60. $R^1 = CH_3$，$R^2 = R^3 = H$
61. $R^1 = R^3 = H$，$R^2 = CH_3$
62. $R^1 = R^2 = H$，$R^3 = CH_3$



63. $R^1 = \beta - OH$，$R^2 = H$
64. $R^1 = \beta - OAc$，$R^2 = H$
65. $R^1 = \alpha - OAc$，$R^2 = H$
66. $R^1 = \beta - OAc$，$R^2 = \beta - CH_2OAc$
67. $R^1 = \beta - OAc$，$R^2 = \alpha - CH_2OAc$
68. $R^1 = \beta - OAc$，$R^2 = \alpha - CH_2OAc$，$\beta - CH_2OAc$
69. $R^1 = \alpha - OAc$，$R^2 = \beta - CH_2OAc$
70. $R^1 = \alpha - OAc$，$R^2 = \alpha - CH_2OAc$



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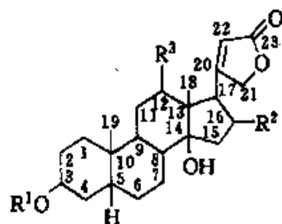


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第二节　心甾内酯类化合物的^{13}C-NMR 化学位移

表 25-4　心甾内酯类化合物 1～10 的^{13}C-NMR 化学位移数据[9]

C \ 化合物	1	2	3	4	5	6	7	8	9	10
1	30.0	30.0	30.0	30.7	30.8	30.8	30.8	30.7	30.0	24.8
2	28.0	28.0	27.9	25.2	25.4	25.3	25.4	27.9	27.9	27.4
3	66.8	66.8	66.8	71.1	71.4	71.3	71.3	66.7	66.6	67.2
4	33.5	33.5	33.4	30.7	30.8	30.8	30.8	33.5	33.3	38.1
5	35.9	36.4	36.4	37.2	37.4	37.4	37.3	36.8	36.4	75.3
6	27.1	27.0	26.9	26.6	26.8	26.8	26.6	26.6	26.9	37.0
7	21.6	21.4	21.2	20.9	21.6	20.6	20.2	24.0	21.9	18.1
8	41.9	41.8	41.8	41.6	41.8	41.5	41.2	36.7	41.3	42.2
9	35.8	35.8	35.9	35.8	36.1	36.2	36.8	45.1	32.6	40.2
10	35.8	35.8	35.6	35.4	35.8	35.5	35.4	36.2	35.5	55.8
11	21.7	21.9	21.3	21.4	21.6	21.2	21.3	21.4	30.0	22.8
12	40.4	41.2	41.0	40.9	40.3	31.3	40.6	37.7	74.8	40.2
13	50.3	50.4	50.7	50.5	50.3	49.5	52.6	54.2	56.4	50.1
14	85.6	85.2	84.1	83.3	85.6	86.1	85.7	146.3	85.8	85.3
15	33.0	42.6	39.5	39.3	33.0	31.3	38.8	108.3	33.0	32.2
16	27.3	72.8	75.0	74.7	27.3	24.8	133.8	135.8	27.9	27.5
17	51.5	58.8	56.8	56.6	51.5	48.9	161.2	158.0	46.1	51.4
18	16.1	16.9	16.1	16.1	16.0	18.5	16.6	20.1	9.4	16.2
19	23.9	23.9	23.9	23.8	23.9	24.0	24.1	24.0	23.8	195.7
20	177.1	171.8	171.5	171.5	171.1	173.6	172.8	173.5	177.1	177.2
21	74.5	76.7	76.8	76.5	74.7	74.8	72.6	72.1	74.6	74.8
22	117.4	119.6	121.3	121.1	117.4	116.6	111.7	119.5	117.0	117.8
23	176.3	175.3	175.8	175.4	176.3	175.8	176.3	176.8	176.3	176.6



1. $R^1 = R^2 = R^3 = H$

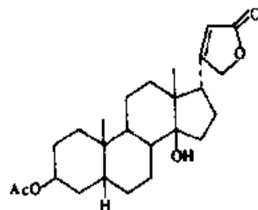
2. $R^1 = R^3 = H$, $R^2 = OH$

3. $R^1 = R^3 = H$, $R^2 = OAc$

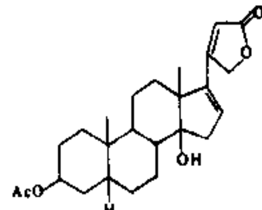
4. $R^1 = Ac$, $R^2 = OAc$, $R^3 = H$

5. $R^1 = Ac$, $R^2 = R^3 = H$

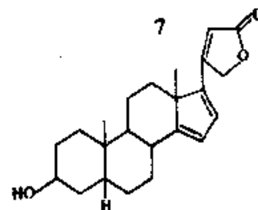
6. $R^1 = R^2 = H$, $R^3 = OH$



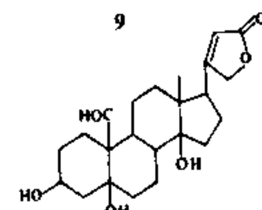
7



9



8

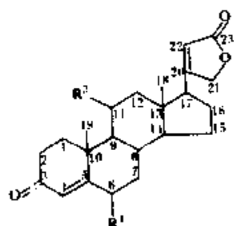


10

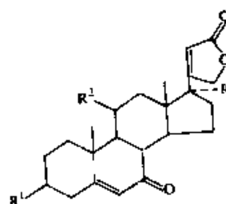
表 25-5 心甾内酯类化合物 11～32 的^{13}C-NMR 化学位移数据[13,14]①

C \ 化合物	11	12	13	14	15	16	17	18	19	20	21
1	35.8	38.1	39.9	36.9	36.1	39.0	36.9	37.9	35.9	32.6	32.1
2	33.9	34.8	35.1	32.1	27.3	31.9	32.1	32.1	27.3	30.7	26.9
3	199.2	199.1	200.2	70.2	70.2	70.6	70.2	71.3	72.0	67.5	71.7
4	124.1	124.7	126.6	42.9	37.8	43.2	42.9	43.4	37.9	40.4	36.6
5	170.4	171.0	170.2	166.9	184.4	167.3	167.0	142.2	165.2	75.6	74.3
6	32.7	33.7	72.8	125.8	126.5	125.1	125.8	120.9	126.5	75.9	76.7
7	31.9	32.0	38.9	200.8	200.7	201.3	201.4	32.9	200.5	34.2	31.5
8	35.9	35.5	29.5	45.8	45.5	45.3	46.3	32.6	43.6	31.1	31.5
9	53.7	59.4	59.8	50.4	49.9	55.7	50.3	58.9	50.0	45.6	45.0
10	38.6	40.4	40.1	38.3	38.5	40.9	38.8	37.0	38.4	38.5	38.0
11	20.9	68.1	68.3	21.4	21.2	67.6	21.2	21.3	21.1	21.3	21.1
12	37.9	49.7	49.9	37.1	37.0	48.2	30.0	38.1	34.5	38.5	38.4
13	44.3	44.6	44.9	45.0	44.9	45.0	49.2	44.4	47.9	45.1	45.0
14	55.8	55.3	55.5	50.3	49.8	49.5	45.1	56.7	50.8	56.2	56.0
15	24.3	24.4	24.6	27.0	26.4	26.5	26.6	24.7	34.2	24.5	24.5
16	25.9	26.1	26.2	26.6	26.4	26.7	38.0	26.2	138.1	26.3	26.2
17	50.7	50.6	50.8	49.9	49.7	49.6	81.7	50.6	144.6	51.3	51.1
18	13.3	14.3	14.3	13.1	13.2	14.0	15.6	13.0	15.8	13.5	13.6
19	17.4	18.4	20.5	17.4	17.3	17.1	17.4	19.6	17.4	16.7	16.5
20	170.8	171.5	171.8	172.1	172.1	172.3	175.3	171.9	158.3	173.2	173.0
21	73.4	73.6	73.7	73.9	73.9	74.0	73.2	73.8	71.5	74.4	74.3
22	116.3	116.3	116.2	116.4	116.4	116.2	116.2	116.1	111.3	115.8	115.9
23	173.9	174.1	174.1	175.4	175.4	174.7	174.1	174.0	174.5	175.7	175.6
CH_3CO					21.0				21.2		21.5
CH_3CO					170.2				170.3		172.0
C \ 化合物	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**
1	31.5	31.5	32.8	34.6	32.7	32.4	31.5	34.1	32.9	32.4	31.9
2	30.4	26.8	28.8	29.7	28.9	30.5	30.4	30.8	30.8	30.5	31.9
3	67.2	71.4	88.2	88.2	88.2	67.0	66.8	66.8	66.6	67.0	66.6
4	38.1	34.7	39.7	40.1	39.7	40.1	38.2	40.4	38.4	40.1	39.5
5	77.1	75.7	66.6	67.3	66.6	74.7	76.0	75.4	76.7	74.8	75.5
6	70.5	74.5	59.7	60.2	59.7	76.8	74.7	76.8	74.7	76.9	74.9
7	34.6	31.0	30.9	31.2	30.8	31.5	31.3	31.5	31.4	31.7	32.2
8	34.3	34.3	30.5	30.3	30.7	31.5	34.4	30.5	33.2	31.7	34.8
9	44.7	44.6	43.0	49.8	42.7	45.2	44.8	51.8	51.3	45.0	45.0
10	39.4	40.2	35.3	36.8	35.2	38.8	40.1	40.4	41.9	38.8	40.5
11	21.3	21.2	20.8	67.4	20.5	21.2	21.3	68.0	68.0	21.0	21.3
12	38.4	38.8	38.0	46.7	30.1	38.5	38.4	49.4	49.5	30.7	30.7
13	45.0	45.0	44.7	44.6	48.5	45.1	45.1	45.0	45.0	49.0	48.9
14	56.2	56.0	57.0	56.0	50.9	56.1	56.0	55.0	55.1	49.9	50.4
15	24.5	24.4	24.4	24.5	23.7	24.6	24.4	24.6	24.5	23.9	23.8
16	26.2	26.2	26.1	26.2	37.1	26.3	26.2	26.2	26.2	37.3	37.4
17	51.1	51.1	50.9	50.6	82.4	51.2	51.1	50.8	50.9	82.7	84.3
18	13.5	13.5	13.3	14.1	15.1	13.7	13.5	14.4	14.4	16.3	15.9
19	15.7	15.8	16.0	16.7	16.0	16.6	15.9	16.8	16.3	16.6	15.9
20	173.0	172.8	172.8	172.8	175.3	173.0	172.6	172.4	172.5	175.5	175.2
21	74.3	74.3	74.3	74.2	73.3	74.4	74.3	74.2	74.3	73.5	73.0
22	115.6	116.0	116.0	116.1	115.6	116.0	116.0	116.1	116.1	115.7	115.9
23	175.6	175.6	175.5	175.5	175.3	175.6	175.7	175.6	175.7	175.5	174.2
CH_3CO		21.5				21.5	21.1	21.5	21.1	21.5	20.8
CH_3CO		172.0				171.4	171.6	171.3	171.7	171.4	170.6

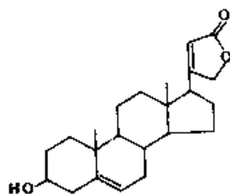
① 化合物 12 在 C_5D_5N 中测定；化合物 13，14，16，17 在 C_5D_5N +（CD_3）CO 中测定；化合物 19～21 在 $CDCl_3$ + CD_3OD 中测定；化合物 22～31 在 $CDCl_3$ + CD_3OD 中测定；化合物 32 在 C_5D_5N 中测定。



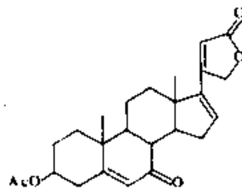
11. $R^1 = R^2 = H$
12. $R^1 = H$, $R^2 = \alpha$-OH
13. $R^1 = \beta$-OH, $R^2 = \alpha$-OH



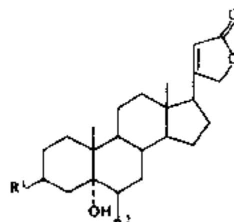
14. $R^1 = \beta$-OH, $R^2 = R^3 = H$
15. $R^1 = \beta$-OAc, $R^2 = R^3 = H$
16. $R^1 = \beta$-OH, $R^2 = \alpha$-OH, $R^3 = H$
17. $R^1 = \beta$-OH, $R^2 = H$, $R^3 = OH$



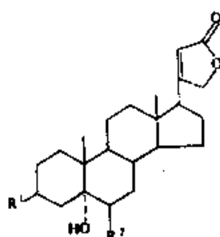
18



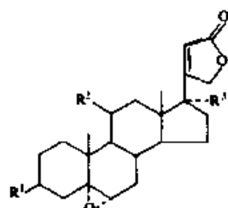
19



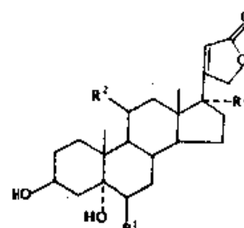
20. $R^1 = \beta$-OH, $R^2 = \beta$-OH
21. $R^1 = \beta$-OAc, $R^2 = \beta$-OAc



22. $R^1 = \beta$-OH, $R^2 = \alpha$-OH
23. $R^1 = \beta$-OAc, $R^2 = \alpha$-OAc
27. $R^1 = \beta$-OH, $R^2 = \beta$-OAc
28. $R^1 = \beta$-OH, $R^2 = \alpha$-OAc



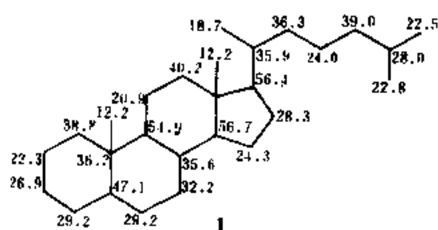
24. $R^1 = \beta$-OH, $R^2 = R^3 = H$
25. $R^1 = \beta$-OH, $R^2 = \alpha$-OH, $R^3 = H$
26. $R^1 = \beta$-OH, $R^2 = H$, $R^3 = OH$



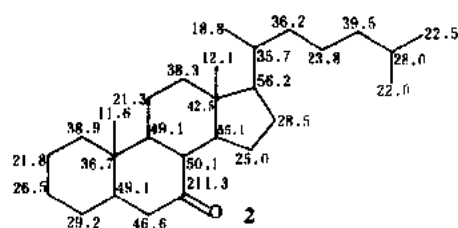
29. $R^1 = \beta$-OAc, $R^2 = \alpha$-OH, $R^3 = H$
30. $R^1 = \alpha$-OAc, $R^2 = \alpha$-OH, $R^3 = H$
31. $R^1 = \beta$-OAc, $R^2 = H$, $R^3 = OH$
32. $R^1 = \alpha$-OAc, $R^2 = H$, $R^3 = OH$

第三节 胆甾烷及胆酸类化合物的^{13}C-NMR 化学位移

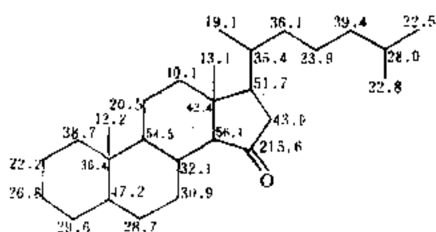
一、胆甾酮类化合物的^{13}C-NMR 化学位移[1]



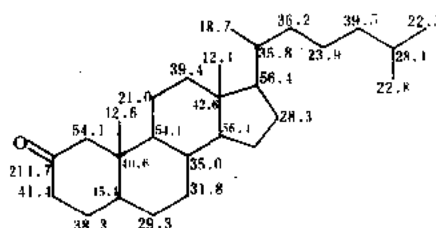
1



2

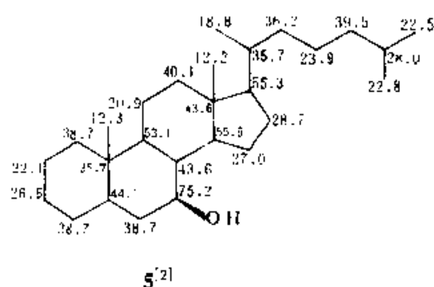


3

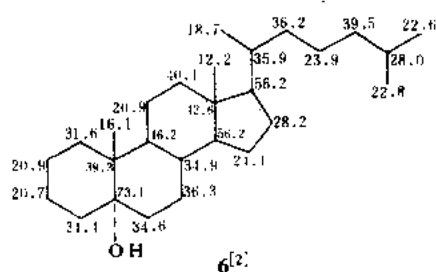


4

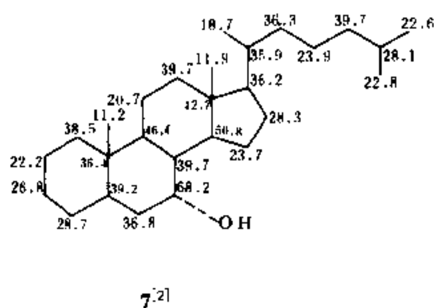
二、胆甾醇类化合物的^{13}C-NMR 化学位移



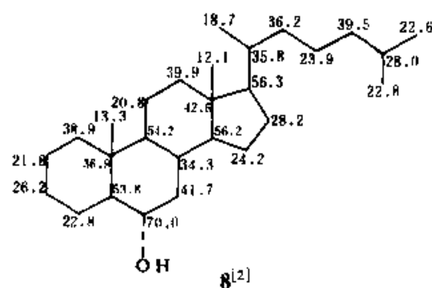
5[2]



6[2]



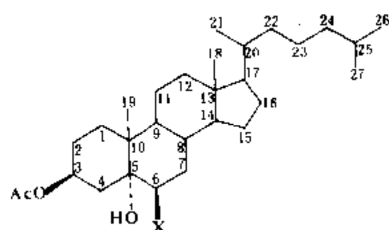
7[2]

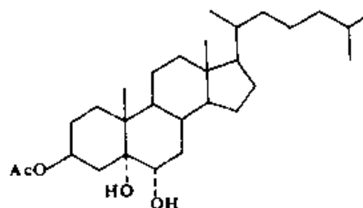


8[2]

表 25-6 胆甾醇类化合物 9 ~ 19 的^{13}C-NMR 化学位移数据[3]

C \ 化合物	9	10	11	12	13	14	15	16	17	18	19
1	30.5	30.6	31.5	32.5	32.9	32.9	33.4	32.2	31.9	31.8	31.0
2	26.8	26.9	26.6	26.6	26.6	26.5	26.9	26.8	26.8	26.8	26.7
3	70.9	70.9	70.8	71.0	71.5	71.5	71.7	71.5	71.0	71.4	71.7
4	40.0	40.1	36.6	38.1	39.1	39.9	38.5	37.0	36.7	37.2	34.4
5	74.9	74.9	74.1	76.6	76.1	75.4	77.2	75.7	74.8	75.8	76.5
6	34.5		95.7	64.0	56.4	34.5	41.8	76.2	76.4	85.7	70.7
7	25.9	25.9	31.9	35.5	36.4	38.6	33.4	34.6	31.5	29.1	35.0
8	34.8	34.8	30.5	30.2	30.6	31.6	30.6	30.3	30.8	30.6	33.7
9	45.6	45.6	44.8	45.5	45.1	45.5	46.0	45.4	44.9	45.4	44.3
10	38.8	38.8	38.1	39.1	39.4	41.5	39.1	38.4	38.5	38.5	39.3
11	21.3	21.4	21.1	21.1	21.2	21.2	21.2	21.2	21.1	21.1	21.2
12	40.0	40.1	39.9	39.9	40.0	40.0	40.0	40.0	40.0	40.0	39.9
13	42.7	42.7	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.8	42.7
14	56.1	56.2	55.8	55.4	55.3	55.1	55.8	55.9	55.9	55.9	55.9
15	24.1	24.1	24.1	24.1	24.1	24.2	24.3	24.2	24.1	24.2	24.2
16	28.3	28.3	28.2	28.2	28.3	28.2	28.2	28.3	28.3	28.2	28.3
17	56.3	56.3	56.4	56.3	56.5	56.4	56.4	56.4	56.4	56.4	56.3
18	12.1	12.1	12.1	12.2	12.2	12.2	12.2	12.2	12.2	12.1	12.1
19	16.1	16.1	15.8	18.3	19.0	20.7	18.3	16.7	16.4	16.1	15.5
20	35.9	35.9	35.9	35.8	35.9	35.8	35.9	35.9	35.9	35.8	35.8
21	18.7	18.7	18.7	18.7	18.7	18.7	18.7	18.7	18.7	18.7	18.7
22	36.2	36.2	36.2	36.2	36.3	36.2	36.2	36.3	36.3	36.2	36.2
23	23.9	24.0	24.0	24.0	24.1	24.0	24.0	24.0	24.1	24.2	24.2
24	39.5	39.6	39.5	39.5	39.5	39.5	39.5	39.6	39.6	39.5	39.6
25	28.0	28.0	28.0	28.0	28.0	28.0	28.0	28.1	28.0	28.0	28.0
26	22.6	22.6	22.6	22.6	22.6	22.6	22.6	22.6	22.6	22.6	22.6
27	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8
$OCOCH_3$	21.3	21.3	21.4	21.4	21.4	21.4	21.4	21.4	21.5	21.5	21.5
其他							17.4		21.5	57.7	





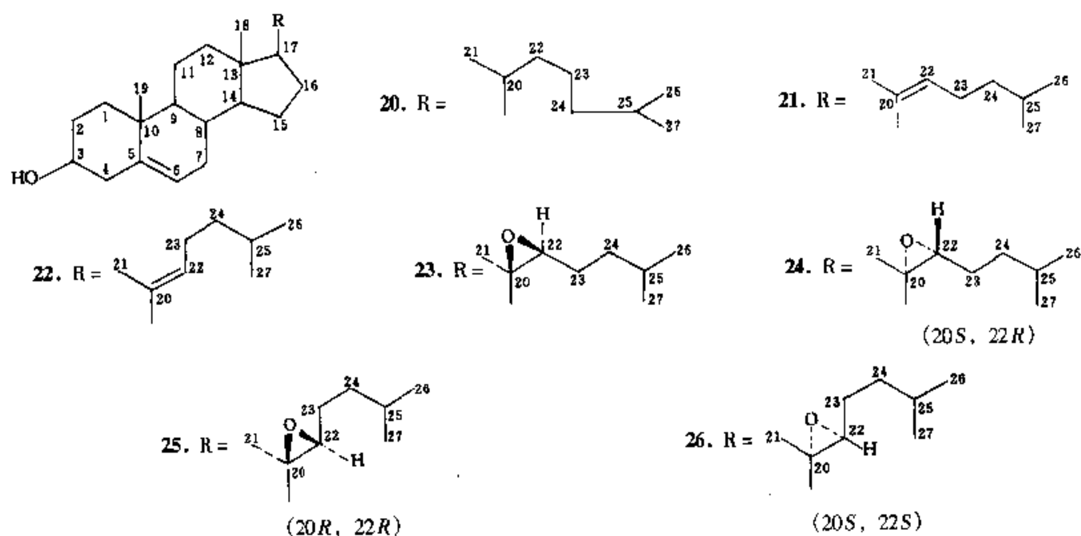
9. X = H
10. X = D
11. X = F
12. X = Cl
13. X = Br
14. X = I
15. X = Me
16. X = OH
17. X = OAc
18. X = OMe

19

三、胆甾烯醇类化合物的^{13}C-NMR化学位移

表 25-7 胆甾烯醇类化合物 20~26 的^{13}C-NMR 化学位移数据[7]

C \ 化合物	20	21	22	23	24	25	26
1	37.3	37.3	37.3	37.4	37.4	37.4	37.4
2	31.6	31.6	31.6	32.1	32.1	32.1	32.1
3	71.6	71.6	71.6	71.8	71.8	71.8	71.8
4	42.2	42.2	42.2	42.4	42.4	42.4	42.4
5	140.6	140.6	140.6	141.0	141.0	141.0	141.0
6	121.7	121.7	121.7	121.8	121.8	121.8	121.8
7	31.9	31.9	31.9	31.9	31.9	31.9	31.9
8	31.9	31.9	31.9	31.9	31.9	31.9	31.9
9	50.2	50.2	50.2	50.4	50.4	50.4	50.4
10	36.5	36.5	36.5	36.6	36.6	36.6	36.6
11	21.1	21.1	21.1	21.0	21.0	21.0	21.0
12	39.8	39.8	39.8	39.8	39.8	39.8	39.8
13	42.3	45.9	43.6	42.5	42.4	43.2	42.5
14	56.8	55.9	56.5	56.4	56.2	56.7	56.8
15	24.3	24.7	24.5	24.3	24.7	23.9	24.1
16	27.9	26.3	26.0	26.9	26.3	26.2	26.6
17	56.3	51.2	59.1	53.3	50.5	56.7	56.8
18	11.9	14.0	13.0	14.7	14.4	13.2	13.5
19	19.4	19.4	18.4	19.4	19.4	19.4	19.4
20	35.8	134.2	134.1	61.1	61.0	60.0	60.4
21	18.8	22.8	17.8	22.6	22.7	17.3	20.3
22	30.2	129.6	126.1	66.5	65.1	60.4	59.8
23	23.9	24.7	24.9	23.4	24.7	21.9	22.4
24	39.5	38.5	38.9	36.4	35.8	35.6	35.7
25	28.0	28.0	28.0	28.0	28.0	28.0	28.0
26	22.6	22.6	22.6	22.6	22.6	22.6	22.6
27	22.6	22.6	22.6	22.6	22.6	22.6	22.6



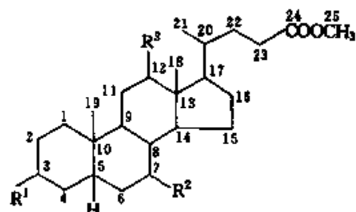
四、胆酸类化合物的¹³C-NMR化学位移

表 25-8 胆酸类化合物 1～29 的¹³C-NMR 化学位移数据[17]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	37.5	35.0	29.8	37.4	37.4	37.2	37.2	37.4	37.1	35.2	29.8	34.8	29.3	35.1	29.7
2	21.2	30.1	27.8	21.1	21.0	21.0	21.0	21.4	21.0	30.5	27.7	30.1	27.2	30.2	27.6
3	26.9	71.0	66.7	27.5	26.7	26.7	26.8	27.5	26.8	71.7	66.7	70.9	65.7	71.4	67.9
4	27.4	36.0	33.4	30.2	28.4	27.2	27.2	29.5	27.1	39.6	36.6	37.2	34.1	36.2	33.3
5	43.6	41.8	36.3	43.0	44.0	43.5	43.1	42.9	43.4	41.5	35.9	42.4	36.7	42.0	36.4
6	27.1	26.9	26.5	35.5	37.1	26.9	26.9	34.1	26.9	34.7	35.5	37.0	36.5	27.1	26.5
7	26.4	26.2	26.1	68.1	71.2	26.0	25.9	71.5	25.9	68.2	68.5	70.9	70.7	26.0	25.9
8	35.7	35.5	35.5	39.2	43.6	35.8	34.4	37.8	35.6	39.3	39.3	43.4	43.0	35.9	35.7
9	40.4	40.1	39.6	32.6	39.1	33.4	39.1	31.6	34.5	32.7	32.0	39.2	38.2	33.3	32.7
10	35.2	34.2	34.9	35.0	34.7	34.6	35.0	35.4	34.2	35.0	34.2	33.9	34.1	33.9	34.5
11	20.7	20.5	20.9	20.3	20.9	28.5	29.3	20.5	25.3	20.5	20.8	21.1	21.1	28.5	28.8
12	40.2	39.9	40.2	39.4	40.1	72.8	79.1	39.5	75.8	39.6	39.6	40.1	39.8	72.8	73.0
13	42.6	42.4	42.6	42.3	43.6	46.2	47.6	42.6	44.8	42.5	42.6	43.6	43.2	46.3	46.4
14	56.5	56.2	56.4	50.1	55.7	48.0	54.4	50.3	49.4	50.3	50.4	55.8	55.6	47.9	48.3
15	24.1	23.9	24.0	23.3	26.9	23.5	23.4	23.5	23.3	23.5	23.6	26.8	26.5	23.6	23.5
16	28.0	27.8	28.0	27.8	27.9	27.2	23.8	27.9	27.1	28.0	28.0	28.4	28.2	27.4	27.4
17	55.8	55.6	55.8	55.5	54.8	49.6	57.2	55.6	47.3	55.7	55.8	54.9	54.5	47.0	47.2
18	11.9	11.7	11.9	11.4	12.0	12.5	7.7	11.6	12.2	11.7	11.7	12.0	11.7	12.5	12.6
19	24.1	23.1	23.7	23.3	24.1	23.7	23.8	23.5	23.7	22.7	23.1	23.3	23.5	22.9	23.5
20	35.2	35.1	35.2	35.0	35.1	34.9	32.4	35.1	34.5	35.2	35.3	35.1	34.8	35.1	35.0
21	18.1	17.9	18.1	17.9	18.2	16.9	20.7	18.1	17.3	18.2	18.2	18.2	18.0	17.1	17.2
22	30.8	30.7	30.8	30.6	30.8	30.7	31.9	30.8	30.7	30.9	30.9	30.9	30.6	31.0	31.0
23	30.8	30.7	30.8	30.6	30.8	30.7	30.9	30.8	30.7	30.9	30.9	30.9	30.6	30.8	30.8
24	174.2	174.2	174.4	174.1	174.3	174.2	174.3	174.3	174.1	174.5	174.5	174.5	174.2	174.5	174.5
25	51.1	51.0	51.2	51.0	51.2	51.1	51.1	51.2	51.1	51.3	51.4	51.3	51.0	51.2	51.4

续表

C \ 化合物	16	17	18	19	20	21	22	23	24	25	26	27	28	29
1	35.2	29.5	37.5	37.2	37.4	37.5	35.3	34.8	34.2	29.8	34.8	29.8	29.3	29.0
2	30.3	27.3	21.2	20.7	21.2	21.1	30.1	30.6	29.1	27.7	30.1	27.7	27.7	27.6
3	71.1	66.1	27.7	26.8	27.5	26.9	71.7	71.1	71.0	66.9	70.6	66.6	66.2	66.1
4	35.9	33.0	30.4	27.8	30.2	28.0	39.4	39.3	36.9	36.6	36.9	36.5	34.3	34.4
5	41.6	35.7	43.1	43.9	42.7	43.8	41.4	41.2	42.6	35.9	42.1	35.7	36.9	36.9
6	26.9	26.3	35.4	36.8	35.1	37.1	34.7	35.2	36.6	35.2	36.9	35.4	36.6	36.7
7	25.8	25.5	68.7	71.7	68.0	71.2	68.3	67.7	71.0	68.5	70.6	68.2	71.0	71.0
8	34.4	33.9	39.5	43.7	37.9	42.3	39.4	38.0	43.5	39.5	42.1	38.0	43.5	42.1
9	39.3	38.3	26.3	31.9	31.9	37.8	26.2	32.0	31.2	25.9	37.9	31.3	31.2	37.2
10	34.2	34.5	35.6	34.1	35.6	34.7	34.7	34.8	33.9	34.3	33.8	34.3	33.9	34.4
11	29.5	29.1	28.1	28.7	29.2	29.0	28.0	29.3	27.7	28.6	29.1	29.3	29.2	29.5
12	79.1	78.9	73.1	72.2	78.8	79.4	73.0	78.9	72.2	72.8	79.1	79.0	72.2	79.3
13	47.8	47.5	46.5	47.1	47.4	48.6	46.3	47.5	47.5	46.6	48.6	47.6	47.5	48.6
14	54.8	54.2	41.5	47.2	48.4	53.9	41.4	48.5	47.2	41.9	54.2	48.6	47.2	53.9
15	23.5	23.3	23.2	26.2	22.9	26.2	23.1	22.9	26.1	23.2	26.2	23.1	26.1	26.2
16	24.0	23.6	27.4	27.6	23.7	23.6	27.4	23.7	27.4	27.4	23.8	23.8	27.4	23.6
17	57.3	57.0	47.1	45.7	56.9	56.5	46.8	57.0	45.7	47.2	56.5	57.1	45.8	56.4
18	7.8	7.5	12.4	12.6	7.5	8.0	12.3	7.6	12.6	12.5	8.0	7.7	12.6	8.0
19	23.0	23.3	23.2	23.8	23.2	24.0	22.3	22.5	23.4	22.9	23.1	23.0	23.4	23.6
20	32.5	32.1	35.3	34.8	32.4	32.3	35.3	32.5	34.8	33.2	32.3	32.6	34.8	32.3
21	20.7	20.5	17.2	17.1	20.8	21.1	17.4	20.9	17.2	17.4	21.0	21.0	17.2	21.1
22	32.0	31.8	31.1	30.8	32.0	32.3	31.0	32.1	30.9	31.1	32.1	32.1	30.9	32.3
23	31.2	31.0	30.8	30.8	30.8	31.2	31.0	30.8	30.9	30.9	31.2	31.2	30.8	31.4
24	174.6	174.4	174.6	174.4	174.5	174.6	174.7	174.7	174.6	174.7	174.8	174.7	174.5	174.7
25	51.2	51.0	51.3	51.2	51.2	51.4	51.4	51.3	51.4	51.4	51.4	51.4	51.3	51.4



1. $R^1 = R^2 = R^3 = H$
2. $R^1 = \alpha$-OH, $R^2 = R^3 = H$
3. $R^1 = \beta$-OH, $R^2 = R^3 = H$
4. $R^1 = R^3 = H$, $R^2 = \alpha$-OH
5. $R^1 = R^3 = H$, $R^2 = \beta$-OH
6. $R^1 = R^2 = H$, $R^3 = \alpha$-OH
7. $R^1 = R^2 = H$, $R^3 = \beta$-OH
8. $R^1 = R^3 = H$, $R^2 = \alpha$-$OCOCH_3$
9. $R^1 = R^2 = H$, $R^3 = \alpha$-$OCOCH_3$
10. $R^1 = R^2 = \alpha$-OH, $R^3 = H$
11. $R^1 = \beta$-OH, $R^2 = \alpha$-OH, $R^3 = H$
12. $R^1 = \alpha$-OH, $R^2 = \beta$-OH, $R^3 = H$
13. $R^1 = R^2 = \beta$-OH, $R^3 = H$
14. $R^1 = R^3 = \alpha$-OH, $R^2 = H$
15. $R^1 = \beta$-OH, $R^2 = H$, $R^3 = \alpha$-OH
16. $R^1 = \alpha$-OH, $R^2 = H$, $R^3 = \alpha$-OH
17. $R^1 = R^3 = \beta$-OH, $R^2 = H$
18. $R^1 = H$, $R^2 = R^3 = \alpha$-OH
19. $R^1 = H$, $R^2 = \beta$-OH, $R^3 = \alpha$-OH
20. $R^1 = H$, $R^2 = \alpha$-OH, $R^3 = \beta$-OH
21. $R^1 = H$, $R^2 = R^3 = \beta$-OH
22. $R^1 = R^2 = R^3 = \alpha$-OH
23. $R^1 = R^2 = \alpha$-OH, $R^3 = \beta$-OH
24. $R^1 = R^3 = \alpha$-OH, $R^2 = \beta$-OH
25. $R^1 = \beta$-OH, $R^2 = R^3 = \alpha$-OH
26. $R^1 = \alpha$-OH, $R^2 = R^3 = \beta$-OH
27. $R^1 = R^3 = \beta$-OH, $R^2 = \alpha$-OH
28. $R^1 = R^2 = \beta$-OH, $R^3 = \alpha$-OH
29. $R^1 = R^2 = R^3 = \beta$-OH

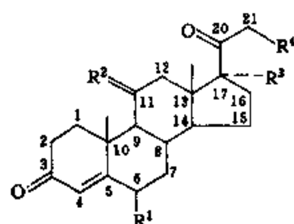
第四节　其他甾族化合物的^{13}C-NMR化学位移

一、孕甾烷类化合物的^{13}C-NMR化学位移

表 25-9　孕甾烷类化合物 1～7 的^{13}C-NMR化学位移数据[15]①

C \ 化合物	1	2	3	4	5	6	7
1	34.0	35.1	35.0	35.2	34.2	34.0	34.0
2	33.4	33.5	33.4	33.4	33.5	33.4	33.4
3	197.8	198.2	197.5	197.4	197.7	197.9	197.7
4	121.5	123.1	123.0	123.0	121.5	121.5	121.4
5	172.1	172.1	170.4	170.4	171.9	172.2	172.0
6	32.4	31.9	31.8	31.9	32.6	32.7	32.7
7	31.3	32.0	31.5	32.1	31.5	31.4	31.3
8	31.0	35.1	34.8	35.2	31.2	31.1	31.1
9	55.6	53.1	52.9	53.0	55.7	55.6	55.5
10	38.8	38.2	38.0	38.1	38.9	38.8	38.8
11	66.2	20.3	20.4	20.3	66.3	66.5	66.4
12	46.8	30.4	37.6	30.1	46.8	39.3	39.0
13	42.7	46.3	43.5	47.0	43.2	45.6	46.2
14	56.8	48.9	55.3	49.9	57.1	51.4	51.5
15	23.9	23.1	23.9	23.2	24.2	23.2	23.3
16	21.8	32.3	22.3	33.4	22.0	31.9	32.9
17	62.9	89.2	57.4	88.4	58.4	89.1	88.3
18	15.3	14.5	13.1	14.5	15.7	16.8	16.8
19	20.3	17.0	16.7	17.0	20.5	20.4	20.4
20	208.1	210.3	209.6	211.3	209.8	209.8	211.4
21	30.9	26.6	68.6	65.9	68.6	26.5	65.8

① 在 $(CD_3)_2SO$ 中测定。

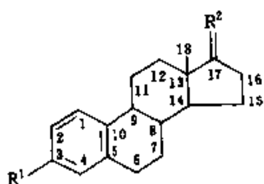


1. $R^1 = R^3 = R^4 = H$，$R^2 = H$，β-OH
2. $R^1 = R^4 = H$，$R^2 = H_2$，$R^3 = OH$
3. $R^1 = R^3 = H$，$R^2 = H_2$，$R^4 = OH$
4. $R^1 = H$，$R^2 = H_2$，$R^3 = R^4 = OH$
5. $R^1 = H$，$R^2 = H$，β-OH，$R^3 = H$，$R^4 = OH$
6. $R^1 = H$，$R^2 = H$，β-OH，$R^3 = OH$，$R^4 = H$
7. $R^1 = H$，$R^2 = H$，β-OH，$R^3 = R^4 = OH$

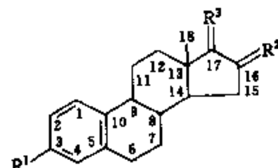
二、雌甾烷类化合物的^{13}C-NMR化学位移

表 25-10 雌甾烷类化合物 1～14 的^{13}C-NMR化学位移数据[16]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	126.0	126.3	126.1	126.2	126.9	126.9	127.2	126.9	126.9	127.0	126.5	127.0	126.9	126.8
2	126.2	126.7	126.4	126.4	113.4	113.5	113.7	119.5	113.5	119.6	112.3	112.3	113.8	112.3
3	126.2	126.7	126.4	126.4	155.6	155.8	155.7	149.8	155.6	149.8	158.7	158.7	156.1	158.4
4	129.7	129.9	129.8	129.7	115.8	115.9	116.1	122.3	115.9	122.3	114.5	174.6	116.0	114.4
5	137.4	137.5	137.5	137.4	138.4	138.2	138.7	138.5	138.4	138.5	138.2	138.8	138.2	138.3
6	30.0	30.0	30.2	30.1	30.1	30.2	30.4	30.1	30.2	30.1	30.4	30.3	30.0	30.5
7	28.8	27.3	28.2	28.2	28.7	27.4	28.9	28.5	28.0	27.8	28.9	28.7	27.4	29.0
8	39.5	39.1	39.7	39.3	39.3	39.3	40.1	39.5	39.8	39.1	39.1	39.8	38.3	39.9
9	45.1	45.4	45.5	45.2	44.6	45.0	44.6	44.6	44.8	44.9	44.7	44.7	44.5	44.6
10	141.5	141.1	141.4	141.2	132.4	131.9	132.6	138.7	132.3	138.6	133.0	133.6	131.5	132.4
11	26.9	26.3	27.1	26.7	27.3	26.4	27.1	26.6	27.1	26.7	27.1	27.0	26.2	26.5
12	39.2	32.6	37.9	37.7	41.5	32.5	33.1	32.6	37.6	37.7	39.1	41.0	31.6	35.9
13	41.4	48.4	44.1	43.7	41.5	48.3	46.2	45.6	43.9	43.7	39.9	39.4	48.7	46.3
14	54.2	51.3	51.3	50.6	54.1	51.1	48.4	50.6	50.8	51.7	51.3	53.7	43.2	47.1
15	25.5	22.2	23.9	23.9	25.6	22.2	24.9	24.8	23.7	23.8	39.1	37.5	36.1	9.7
16	20.9	35.9	31.3	28.1	20.9	35.9	32.4	30.5	31.0	28.2		71.3	204.5	
17	40.9	218.9	81.9		39.5	219.3	79.7	82.2	81.9	83.0	56.2	52.2	204.6	
18	17.6	13.9	11.6	12.5	17.6	13.9	17.5	16.8	11.5	12.4	19.8	19.3	13.7	17.7
CH_3CO				20.8				20.7		20.8				
其 他											55.1			55.2



1. $R^1 = H$，$R^2 = H_2$
2. $R^1 = H$，$R^2 = O$
3. $R^1 = H$，$R^2 = H$，β-OH
4. $R^1 = H$，$R^2 = H$，β-OAc
5. $R^1 = OH$，$R^2 = H_2$
6. $R^1 = OH$，$R^2 = O$
7. $R^1 = OH$，$R^2 = H$，α-OH
8. $R^1 = OAc$，$R^2 = H$，α-OAc
9. $R^1 = OH$，$R^2 = H$，β-OH
10. $R^1 = OAc$，$R^2 = H$，β-OAc



11. $R^1 = OCH_3$，$R^2 = O$，$R^3 = H_2$
12. $R^1 = OCH_3$，$R^2 = H$，β-OH，$R^3 = H_2$
13. $R^1 = OH$，$R^2 = R^3 = O$
14. $R^1 = OCH_3$，$R^2 = R^3 = H$，α-OH

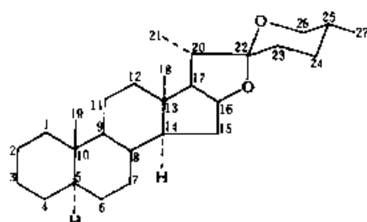
三、螺甾烷类化合物的^{13}C-NMR化学位移

表 25-11 螺甾烷类化合物 1～8 的^{13}C-NMR化学位移数据[9]

C \ 化合物	1	2	3	4	5	6	7	8
1	38.7	37.0	38.6	39.7	37.2	36.5	29.9	29.9
2	22.2	31.5	22.2	125.7	31.6	31.2	27.8	27.8
3	26.8	71.2	26.8	125.5	71.5	70.7	67.0	67.0
4	29.0	38.2	29.0	28.7	42.2	37.8	33.6	33.6
5	47.1	44.9	47.0	41.6	140.8	44.6	36.6	36.5
6	29.0	28.6	29.0	30.3	121.3	28.3	26.5	26.6
7	32.4	32.3	32.4	31.4	32.0	31.4	26.5	26.6
8	35.2	35.2	35.2	31.2	31.4	34.4	35.3	35.3
9	54.8	54.4	54.8	54.6	50.1	55.5	40.3	40.3
10	36.3	35.6	36.4	34.9	36.6	36.0	35.3	35.3
11	20.7	21.1	20.6	21.0	20.9	37.8	20.9	20.9
12	40.2	40.1	40.1	42.6	39.8	213.0	39.9	39.9
13	40.6	40.6	40.6	40.7	40.2	55.0	40.7	40.6

续表

C \ 化合物	1	2	3	4	5	6	7	8
14	56.5	56.3	56.5	61.3	56.5	55.8	56.5	56.4
15	31.8	31.8	31.7	69.6	31.8	31.5	31.8	31.7
16	80.8	80.7	81.3	82.1	80.7	79.1	80.9	80.9
17	62.3	62.2	62.0	60.7	62.1	53.5	62.4	62.1
18	16.5	16.5	16.5	19.1	16.3	16.0	16.4	16.5
19	12.3	12.4	12.3	11.7	19.4	12.0	23.8	23.9
20	41.6	41.6	41.5	42.6	41.6	42.2	41.6	42.1
21	14.5	14.5	14.4	14.2	14.5	13.2	14.4	14.3
22	109.0	109.0	108.8	109.9	109.1	109.0	109.1	109.5
23	31.4	31.4	24.7	31.4	31.4	31.2	31.4	27.1
24	28.9	28.8	32.7	28.6	28.8	28.8	28.8	25.8
25	30.3	30.3	66.6	30.2	30.3	30.2	30.3	26.0
26	66.7	66.7	68.9	67.1	66.7	66.8	66.8	65.0
27	17.1	17.1	27.0	17.1	17.1	17.1	17.1	16.1

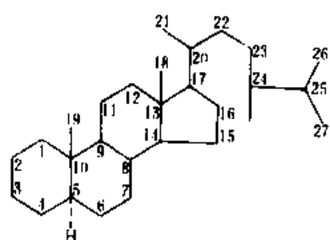


1. (25*R*) -5α-螺甾烷
2. (25*R*) -5α-螺甾-3-醇
3. (25*S*) -5α-螺甾-25-醇
4. Δ^2- (25*R*) -5α-螺甾-15β-醇
5. Δ^2- (25*R*) -5α-螺甾-3β-醇
6. 3β-羟基- (25*R*) -5α-螺甾-12-酮
7. (25*R*) -5β-螺甾-3β-醇
8. (25*S*) -5β-螺甾-5β-醇

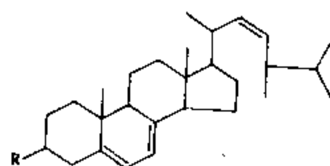
四、麦角甾烷类化合物的^{13}C-NMR 化学位移

表 25-12 麦角甾烷类化合物 1～9 的^{13}C-NMR 化学位移数据[18～20]

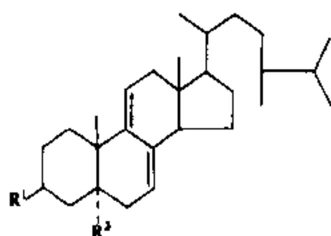
C \ 化合物	1	2	3	4	5	6	7	8	9
1	38.8	38.9	37.9	34.6	34.3	29.7	29.4	28.8	28.5
2	22.2	32.5	28.1	31.6	27.6	30.8	27.0	30.9	26.7
3	26.7	70.0	72.7	70.3	73.1	67.0	70.4	70.0	72.3
4	29.2	41.5	36.6	37.7	33.6	41.8	38.1	37.5	33.4
5	47.2	140.9	138.3	39.1	39.1	73.6	73.3	36.7	36.7
6	29.2	119.7	120.0	29.8	29.8	37.4	37.4	29.7	29.4
7	32.3	117.0	116.2	118.0	118.0	115.8	115.8	125.3	124.9
8	35.6	141.0	141.2	135.7	135.7	136.3	136.3	134.5	134.9
9	54.9	46.8	46.0	143.7	143.4	140.1	140.1	64.5	64.1
10	36.4	37.5	37.1	35.6	33.6	41.1	41.1	34.6	34.6
11	20.9	21.5	21.1	118.8	118.8	122.8	122.8	55.2	54.8
12	40.3	39.7	39.0	42.1	42.1	42.3	42.3	40.2	40.5
13	42.6	43.3	42.8	42.7	42.7	42.3	42.3	42.9	42.9
14	56.6	54.9	54.5	51.5	51.5	51.2	51.2	46.8	46.8
15	24.4	23.4	23.0	23.1	23.1	23.1	23.1	22.4	22.4
16	28.3	28.6	28.1	28.8	28.8	28.7	28.7	28.3	28.3
17	56.3	56.3	55.7	56.0	56.0	55.9	55.9	56.1	56.1
18	12.4	12.1	12.1	11.4	11.4	11.4	11.4	13.7	13.7
19	12.6	18.3	18.1	19.3	19.3	25.0	24.5	15.6	15.6
20	36.4	40.8	40.4	40.3	40.3	40.2	40.2	40.1	40.1
21	18.9	20.3	21.1	20.6	20.6	20.6	20.6	20.8	20.8
22	33.9	136.3	135.4	135.0	135.0	134.8	134.8	134.7	134.7
23	30.9	132.5	131.8	131.5	131.5	131.7	131.7	131.7	131.7
24	39.3	43.4	42.8	42.7	42.7	42.7	42.7	42.7	42.7
25	31.5	33.5	33.0	32.9	32.9	32.8	32.8	32.8	32.8
26	20.6	19.7	19.7	19.6	19.6	19.6	19.6	19.7	19.7
27	17.7	20.0	20.0	19.8	19.8	19.8	19.8	19.8	19.8
CH_3CO			21.2		21.2		21.2		21.2
CH_3CO			170.1		169.7		169.7		169.7
其 他	14.4	17.7	17.8		17.6	17.6	17.6	17.6	17.6



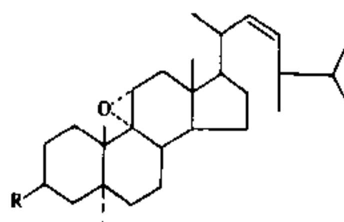
1



2. R = β-OH
3. R = β-OAc

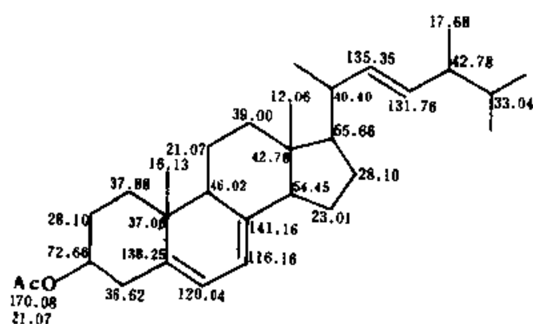


4. R^1 = β-OH, R^2 = H
5. R^1 = β-OAc, R^2 = H
6. R^1 = β-OH, R^2 = OH
7. R^1 = β-OAc, R^2 = OH

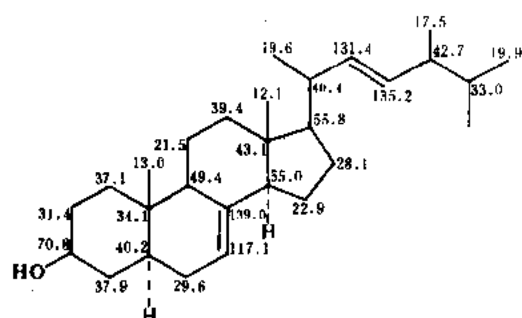


8. R = β-OH
9. R = β-OAc

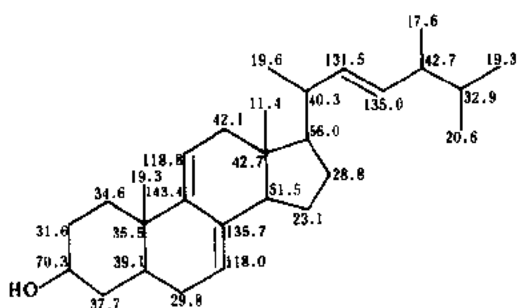
五、其他类甾族化合物的^{13}C-NMR化学位移



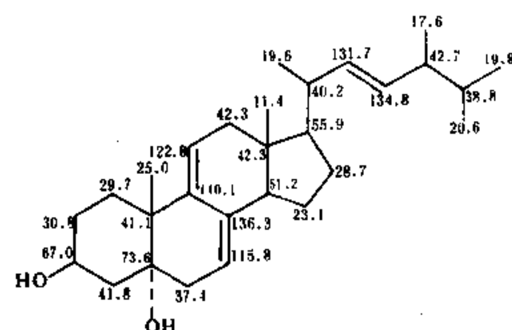
1[4]



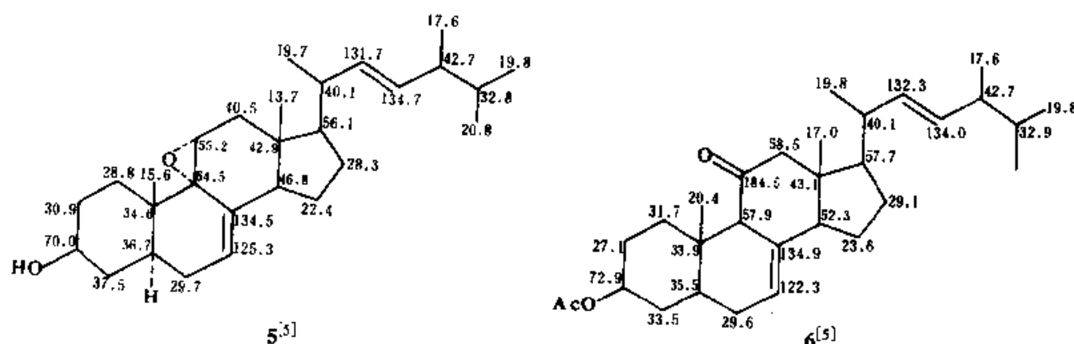
2[5]



3[5]



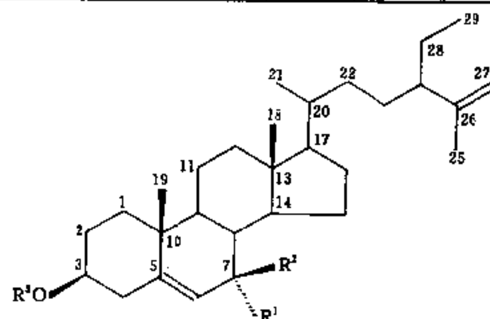
4[5]



5[5]　　6[5]

表 25-13　植物甾醇 7~11 的^{13}C-NMR 化学位移数据[21]

C \ 化合物	7	8	9	10	11	C \ 化合物	7	8	9	10	11
1	36.9	36.8	36.3	37.4	37.2	16	29.3	29.4	29.3	28.2	28.2
2	31.2	31.5	31.1	31.5	31.7	17	55.7	55.3	54.6	56.2	56.1
3	71.0	71.4	70.4	71.7	79.2	18	11.6	11.7	11.6	11.8	11.5
4	41.6	41.6	41.7	42.2	39.6	19	19.8	19.1	17.2	19.4	19.1
5	142.3	143.4	164.9	141.0	140.2	20	36.3	35.4	35.4	35.4	35.4
6	124.1	125.3	126.1	121.8	122.1	21	18.6	18.6	18.7	18.6	18.4
7	65.4	73.3	202.5	33.6	33.6	22	33.6	33.6	33.3	33.7	33.5
8	37.2	40.8	45.3	31.8	31.9	23	29.9	29.6	29.6	29.6	29.4
9	42.1	48.2	49.9	50.3	50.1	24	49.4	49.4	49.4	49.5	49.4
10	36.2	36.2	38.6	36.4	36.5	25	17.7	17.7	17.8	17.8	17.4
11	20.9	21.0	21.1	21.3	20.9	26	147.6	147.6	147.5	147.6	147.5
12	39.8	39.5	38.6	39.7	38.8	27	111.3	111.3	111.3	111.4	111.3
13	42.8	42.8	43.0	42.3	42.2	28	26.9	26.3	26.4	26.4	26.3
14	49.4	55.9	49.8	56.9	56.4	29	11.8	11.9	11.9	12.1	11.8
15	26.4	26.4	26.2	24.3	24.1						



7. $R^1 = OH$, $R^2 = R^3 = H$
8. $R^1 = R^3 = H$, $R^2 = OH$
9. $R^1 = R^2 = O$, $R^3 = H$
10. $R^1 = R^2 = R^3 = H$
11. $R^1 = R^2 = H$, $R^3 = Gal$

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第二十六章　碳水化合物和核苷、氨基酸的^{13}C-NMR化学位移

糖的^{13}C-NMR化学位移研究对了解糖和甙的构型、构象，以及多糖和甙中单糖的连接顺序有着十分重要意义。单糖的^{13}C-NMR化学位移具有如下一些特征。

① 糖分子中C-1羟基甲基化后，形成甲基甙，使C-1的δ值向低磁场位移。甲基α-D-葡萄糖的C-1的化学位移向低场位移7.75个δ单位，甲基β-D-葡萄糖的C-1的化学位移向低场位移7.7个δ单位，甲基α-D-半乳糖的C-1的化学位移向低场位移7.15个δ单位，甲基β-D-半乳糖的C-1的化学位移向低场位移7.4个δ单位，甲基α-D-阿拉伯吡喃糖的C-1的化学位移向低场位移7.75个δ单位，甲基β-D-阿拉伯吡喃糖的C-1的化学位移向低场位移7.35个δ单位。

② 端基碳成甙后，对C-2、3、4的化学位移值影响不太大，一般在2个δ单位之内。

③ 糖分子中，除端基碳外其他位的羟基甲基化后，使该位置碳的δ值移向低场。如：3-*O*-甲基-α-D-葡萄糖的C-3的δ值向低场位移10.15个δ单位，3-*O*-甲基-β-D-葡萄糖的C-3的δ值向低场位移9.65个δ单位。若糖分子中，C-2、3、4、5位与其他糖相连接，也使该位置的碳的化学位移移向低场。

④ 吡喃糖和呋喃糖，因五元杂环和六元杂环结构不同，各个碳的化学位移也不同。

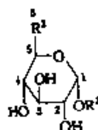
⑤ 糖中羟基被乙酰化后，乙酰基对各碳的影响不同。全乙酰化的α-D-葡萄糖和全乙酰化β-D-葡萄糖的C-1、2、3、4、5化学位移均向高场位移，其中C-1化学位移向高场位移最大。

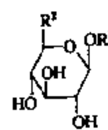
第一节　糖类化合物的^{13}C-NMR化学位移

一、单糖类化合物的^{13}C-NMR化学位移

表26-1　吡喃葡萄糖及其衍生物1～11的^{13}C-NMR化学位移数据[1]

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
1	92.7	96.5	100.3	104.3	93.1	96.8	100.3	100.7	104.3	100.8	104.6
2	72.1	74.8	72.5	74.2	72.9	75.6	76.2	71.9	73.8	71.9	73.7
3	73.4	76.4	74.2	76.9	73.6	76.6	73.9	73.8	76.5	73.7	76.3
4	70.4	70.3	70.6	70.8	76.4	76.1	76.2	72.5	72.3	72.4	72.4
5	72.1	76.6	72.7	76.9	68.8	73.0	68.7	71.9	75.6	71.9	75.7
6	61.3	61.5	61.7	61.9	18.0	18.0	17.6				
OCH_3			56.2	58.3			56.2	56.7	58.5	56.8 54.2	58.7 56.5





1. $R^1=H$, $R^2=CH_2OH$　　**2.** $R^1=H$, $R^2=CH_2OH$

3. $R^1=CH_3$, $R^2=CH_2OH$　　**4.** $R^1=CH_3$, $R^2=CH_2OH$

5. $R^1=H$, $R^2=CH_3$　　**6.** $R^1=H$, $R^2=CH_3$

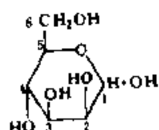
7. $R^1=CH_3$, $R^2=CH_3$　　**9.** $R^1=CH_3$, $R^2=COOH$

8. $R^1=CH_3$, $R^2=COOH$　　**11.** $R^1=CH_3$, $R^2=COOCH_3$

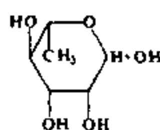
10. $R^1=CH_3$, $R^2=COOCH_3$

表 26-2 甘露糖、鼠李糖、半乳糖、岩藻糖及其衍生物 12～25 的^{13}C-NMR 化学位移数据[1]

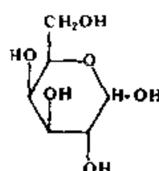
C＼化合物	12	13	14	15	16	17	18	19	20	21	22	23	24	25
1	95.0	94.6	101.9	95.0	94.6	101.9	93.6	97.7	100.5	104.9	93.3	97.3	100.5	104.8
2	71.7	72.3	71.2	71.9	72.4	71.4	69.8	73.3	69.4	71.8	69.2	72.8	69.0	71.5
3	71.3	74.1	71.8	71.1	73.8	71.3	70.5	74.2	70.6	73.9	70.4	74.0	70.6	74.1
4	68.0	67.8	68.0	73.3	72.9	73.1	70.6	70.1	70.4	69.8	73.0	72.5	72.9	72.4
5	73.4	77.2	73.7	69.4	73.1	69.4	71.7	76.3	71.8	76.2	67.4	71.9	67.5	71.9
6	62.1	62.1	62.1	18.0	18.0	17.7	62.5	62.3	62.3	62.1	16.7	16.7	16.5	16.5
OCH_3			55.9			55.8			56.3	58.3			56.3	58.3



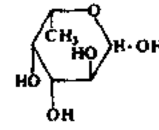
12. α-D-吡喃甘露糖
13. β-D-吡喃甘露糖
14. α-甲基-D-吡喃甘露糖甙



15. α-L-吡喃鼠李糖
16. β-L-吡喃鼠李糖
17. α-甲基-L-吡喃鼠李糖甙



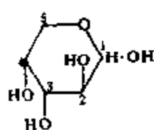
18. α-D-吡喃半乳糖
19. β-D-吡喃半乳糖
20. α-甲基-D-吡喃半乳糖甙
21. β-甲基-D-吡喃半乳糖甙



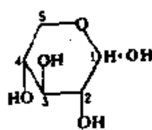
22. α-L-吡喃岩藻糖
23. β-L-吡喃岩藻糖
24. α-甲基-L-吡喃岩藻糖
25. β-甲基-L-吡喃岩藻糖

表 26-3 吡喃阿拉伯糖、吡喃木糖、呋喃半乳糖、呋喃核糖、呋喃阿拉伯糖及其衍生物 26～39 的^{13}C-NMR 化学位移数据[1]

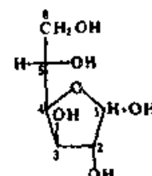
C＼化合物	26	27	28	29	30	31	32	33	34	35	36	37	38	39
1	97.8	93.7	105.1	101.0	93.3	97.6	100.6	105.1	103.1	109.2	104.2	109.0	109.5	103.3
2	73.0	69.6	71.8	69.4	72.5	75.1	72.3	74.0	77.4	81.9	72.1	75.3	82.0	76.3
3	73.5	69.8	73.4	69.9	73.9	76.9	74.3	76.0	75.5	77.8	70.8	71.9	77.9	77.9
4	69.6	69.8	69.4	70.0	70.4	70.3	70.4	70.4	82.3	84.0	85.5	83.9	84.8	83.1
5	67.5	63.6	67.3	63.8	62.1	66.3	62.0	66.3	73.7	72.0	62.2	63.9	62.5	63.7
6									63.4	63.9				
OCH_3			58.1	56.3			56.0	58.3	56.1	56.1	56.5	56.3	55.6	56.1



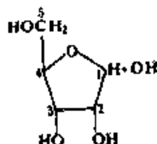
26. α-L（或 D）-吡喃阿拉伯糖
27. β-L（或 D）-吡喃阿拉伯糖
28. α-甲基-L（或 D）-吡喃阿拉伯糖甙
29. β-甲基-L（或 D）-吡喃阿拉伯糖甙



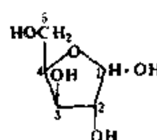
30. α-D-吡喃木糖
31. β-D-吡喃木糖
32. α-甲基-D-吡喃木糖甙
33. β-甲基-D-吡喃木糖甙



34. α-甲基-D-呋喃半乳糖甙
35. β-甲基-D-呋喃半乳糖甙



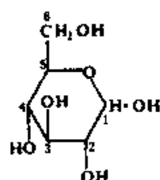
36. α-甲基-D-呋喃核糖甙
37. β-甲基-D-呋喃核糖甙



38. α-甲基-L-呋喃阿拉伯糖甙
39. β-甲基-L-呋喃阿拉伯糖甙

表 26-4 吡喃葡萄糖衍生物 40 ~ 47 的 ^{13}C-NMR 化学位移数据[2]

C \ 化合物	40	41	42	43	44	45	46	47
1	90.7	97.1	93.4	97.2	93.2	97.1	93.3	97.3
2	81.9	85.2	72.6	75.1	73.0	75.8	73.0	75.8
3	73.5	76.8	84.1	86.7	73.9	76.7	74.3	77.2
4	71.3	71.3	70.6	70.4	80.5	80.5	71.4	71.4
5	72.8	77.3	72.8	77.3	71.7	76.1	71.4	75.8
6	62.4	62.4	62.3	62.3	62.1	62.1	72.6	72.6
OCH_3	59.3	61.7	61.3	61.3	61.6	61.6	60.3	60.3

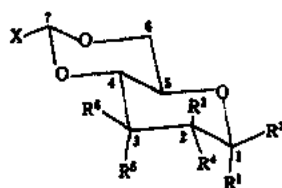


40. 2-*O*-甲基-α-D-吡喃葡萄糖
41. 2-*O*-甲基-β-D-吡喃葡萄糖
42. 3-*O*-甲基-α-D-吡喃葡萄糖
43. 3-*O*-甲基-β-D-吡喃葡萄糖
44. 4-*O*-甲基-α-D-吡喃葡萄糖
45. 4-*O*-甲基-β-D-吡喃葡萄糖
46. 6-*O*-甲基-α-D-吡喃葡萄糖
47. 6-*O*-甲基-β-D-吡喃葡萄糖

表 26-5 己糖衍生物 48 ~ 61 的 ^{13}C-NMR 化学位移数据[3]①

C \ 化合物	48	49	50	51	52	53	54	55	56	57	58	59	60	61
1	100.2	101.6	99.4	99.9	104.2	101.7	98.1	100.5	98.9	99.4	101.6	100.8	102.0	104.1
2	67.9	69.6	70.8	72.4	74.2	70.6	29.0	67.4	67.0	72.1	69.4	67.5	70.0	74.2
3	68.8	68.8	68.6	70.5	72.9	68.0	23.5	31.4	32.6	52.4	52.0	52.1	50.3	72.9
4	78.1	76.0	76.5	80.8	80.3	78.5	77.9	73.5	76.1	81.0	75.9	78.3	79.4	79.8
5	56.9	57.8	62.8	62.0	65.9	62.0	64.5	64.6	63.4	62.2	57.6	56.7	63.4	65.9
6	68.8	68.8	68.6	68.5	68.3	68.4	69.1	68.9	68.9	68.7	68.8	68.9	68.5	67.7
7	101.5	101.8	101.8	101.5	101.5	101.7	101.6	101.8	101.3	105.5	101.8	101.3	101.6	99.4
OCH_3	55.7	55.0	56.4	54.9	56.8	54.4	54.2	54.3	54.6	55.0	54.8	55.6	54.5	56.7

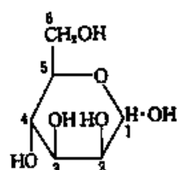
① 以 $CDCl_3 + CD_3OD$ 体积比 = 4:1 为溶剂。



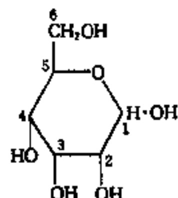
化合物	己糖构型	R^1	R^2	R^3	R^4	R^5	R^6
48	α-allo	OCH_3	H	H	OH	OH	H
49	α-altro	OCH_3	H	OH	H	OH	H
50	β-altro	H	OCH_3	OH	H	OH	H
51	α-glu	OCH_3	H	H	OH	H	OH
52	β-glu	H	OCH_3	H	OH	H	OH
53	α-man	OCH_3	H	OH	H	H	OH
54	2, 3-二去氧-α-erythro	OCH_3	H	H	H	H	H
55	3-去氧-α-arab	OCH_3	H	OH	H	H	H
56	3-去氧 α-ribo	OCH_3	H	H	OH	H	H
57	α-glu	OCH_3	H	H	OH	H	NH_2
58	α-altro	OCH_3	H	OH	H	NH_2	H
59	α-allo	OCH_3	H	H	OH	NH_2	H
60	α-man	OCH_3	H	OH	H	H	NH_2
61	β-glu	H	OCH_3	H	OH	H	OH

表 26-6　吡喃甘露糖衍生物及吡喃阿洛糖 62～71 的^{13}C-NMR 化学位移数据[4]

C \ 化合物	62	63	64	65	66	67	68	69	70	71
1	101.1	91.8	95.0	95.0	94.7	94.9	94.6	94.7	93.4	94.0
2	71.4	81.6	82.6	67.3	68.1	71.9	72.1	73.2	67.6	71.9
3	74.0	71.0	74.5	80.0	83.2	71.1	73.9	74.1	72.3	71.7
4	67.9	68.3	68.0	66.8	66.6	77.9	77.7	67.8	66.7	67.4
5	77.4	73.3	77.5	73.4	77.3	72.4	76.3	75.8	67.5	74.2
6	62.2	62.1	62.1	62.0	62.0	61.8	61.8	72.0	61.4	61.8



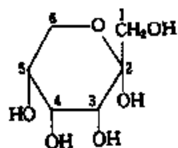
62. β-甲基-D-吡喃甘露糖甙
63. 2-*O*-甲基-α-D-吡喃甘露糖
64. 2-*O*-甲基-β-D-吡喃甘露糖
65. 3-*O*-甲基-α-D-吡喃甘露糖
66. 3-*O*-甲基-β-D-吡喃甘露糖
67. 4-*O*-甲基-α-D-吡喃甘露糖
68. 4-*O*-甲基-β-D-吡喃甘露糖
69. 6-*O*-甲基-β-D-吡喃甘露糖



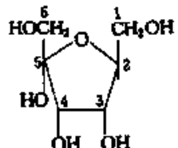
70. α-D-吡喃阿洛糖
71. β-D-吡喃阿洛糖

表 26-7　吡喃阿洛酮糖及其衍生物和呋喃阿洛酮糖及其衍生物 72～80 的^{13}C-NMR 化学位移数据[5]

C \ 化合物	72	73	74	75	76	77	78	79	80
1	65.0	65.0	66.1	64.2	63.3	61.4	58.2	61.6	60.1
2	99.1	98.4	103.3	104.0	106.3	106.2	110.2	106.2	110.8
3	66.4	71.2	70.5	71.2	75.6	73.4	75.6	73.3	75.4
4	65.9	71.2	70.8	72.6	71.9	71.7	72.8	71.9	73.4
5	69.8	66.7	66.5	84.3	84.3	85.7	84.6	83.6	82.9
6	62.2	58.9	58.7	64.2	63.6	63.1	64.4	73.7	75.4
OCH_3						50.2	52.6	50.2 (1)	50.5 (1)
								60.2 (6)	58.5 (6)



72. α-D-吡喃阿洛酮糖
73. β-D-吡喃阿洛酮糖
74. β-甲基-D-吡喃阿洛酮糖甙



75. α-D-呋喃阿洛酮糖
76. β-D-呋喃阿洛酮糖
77. α-甲基-D-呋喃阿洛酮糖甙
78. β-甲基-D-呋喃阿洛酮糖甙
79. α-甲基-6-*O*-甲基-D-呋喃阿洛酮糖甙
80. β-甲基-6-*O*-甲基-D-呋喃阿洛酮糖甙

二、二糖的^{13}C-NMR 化学位移

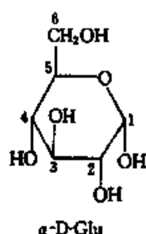
表 26-8　葡萄二糖类化合物 1～24 的^{13}C-NMR 化学位移数据[2]①

C \ 化合物	1	2	3	4	5	6	7	8	9	10	11	12
1	94.8	100.7	101.3	90.8	97.5	105.0	93.1	95.8	100.0	93.1	97.0	93.4
2	73.9	74.2	74.0	77.1	79.9	79.0	82.1	82.8	81.7	71.3	74.1	72.2
3	74.4	77.3	74.6	73.1	75.8	75.8	73.2	77.2	73.3	80.8	83.2	84.2
4	73.5	71.1	70.9	71.1	71.1	70.8	71.1	71.1	71.3	70.6	70.6	69.6
5	72.3	77.3	72.9	73.1	77.1	77.1	72.5	77.2	72.5	72.2	76.6	72.4
6	62.5	62.5	62.0	62.0	62.0	62.5	62.4	62.4	62.2	61.8	61.8	62.4
1′			104.0	97.5	99.0	99.0	105.1	103.9	105.0	99.8	99.8	103.9
2′			74.3	73.1	73.1	73.0	74.9	74.9	74.4	72.8	72.8	74.8
3′			77.4	74.4	74.4	74.2	77.2	77.2	77.1	74.1	74.1	77.1
4′			70.9	71.1	71.1	71.3	71.1	71.1	71.3	71.3	71.3	71.2
5′			76.8	73.1	73.1	73.0	77.2	77.2	77.1	72.8	72.8	77.1
6′			62.3	62.0	62.0	61.9	62.4	62.4	62.2	61.8	61.8	62.4
OCH_3						58.9			56.2			

续表

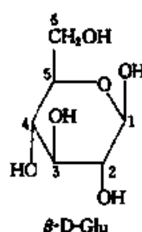
C \ 化合物	13	14	15	16	17	18	19	20	21	22	23	24
1	97.2	93.2	97.1	104.4	93.2	97.1	104.5	93.8	97.7	93.3	97.2	104.5
2	74.8	73.0	75.7	74.6	72.9	75.7	74.2	73.3	75.9	72.9	75.5	74.0
3	86.7	74.6	77.8	77.8	72.9	76.1	76.4	75.0	77.7	74.5	77.1	77.0
4	69.6	78.5	78.5	78.7	80.1	80.1	80.3	71.3	71.3	71.1	71.1	71.2
5	77.1	71.6	76.1	76.1	71.6	75.7	75.9	71.3	75.9	71.8	76.1	76.1
6	62.4	62.5	62.5	62.3	61.8	61.8	61.8	67.4	67.4	70.2	70.2	70.0
1′	103.9	101.0	101.0	101.1	103.9	103.9	103.9	99.4	99.4	103.8	103.8	104.0
2′	74.8	74.3	74.3	74.3	74.7	74.7	74.6	73.3	73.3	74.5	74.5	74.0
3′	77.1	74.6	74.6	74.6	77.4	77.4	77.5	75.0	75.0	77.1	77.1	77.2
4′	71.2	71.0	71.0	70.9	71.1	71.2	71.2	71.3	71.3	71.1	71.1	71.0
5′	77.1	73.4	73.4	73.4	77.2	77.2	77.2	73.8	73.8	77.1	77.1	77.1
6′	62.4	62.5	62.5	62.3	62.4	62.4	62.4	62.5	62.5	62.5	62.5	62.5
OCH_3				58.7			58.9					58.8

① 以 D_2O 为溶剂。



α-D-Glu

1. α-D-Glu 1－1α-D-Glu′
2. β-D-Glu 1－1β-D-Glu′
3. α-D-Glu 1－1β-D-Glu′
4. α-D-Glu 2－1α-D-Glu′
5. β-D-Glu 2－1α-D-Glu′
6. β-CH_3-D-Glu 2－1α-D-Glu′
7. α-D-Glu 2－1β-D-Glu′
8. β-D-Glu 2－1β-D-Glu′
9. α-CH_3-D-Glu 2－1β-D-Glu′
10. α-D-Glu 3－1α-D-Glu′
11. β-D-Glu 3－1α-D-Glu′
12. α-D-Glu 3－1β-D-Glu′



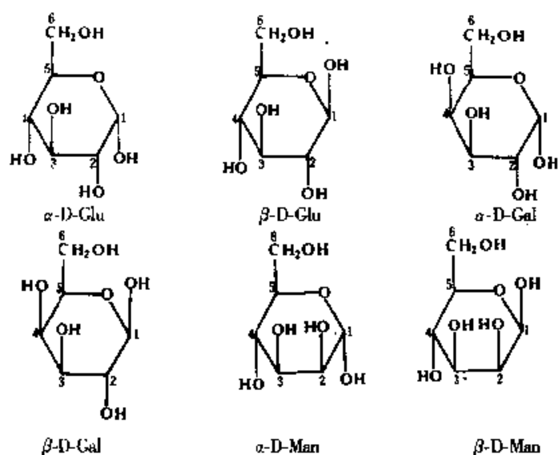
β-D-Glu

13. β-D-Glu 3－1β-D-Glu′
14. α-D-Glu 4－1α-D-Glu′
15. β-D-Glu 4－1α-D-Glu′
16. β-CH_3-D-Glu 4－1α-D-Glu′
17. α-D-Glu 4－1β-D-Glu′
18. β-D-Glu 4－1β-D-Glu′
19. β-CH_3-D-Glu 4－1β-D-Glu′
20. α-D-Glu 6－1α-Glu′
21. β-D-Glu 6－1α-D-Glu′
22. α-D-Glu 6－1β-D-Glu′
23. β-D-Glu 6－1β-D-Glu′
24. β-CH_3-D-Glu 6－1β-D-Glu′

表 26-9 其他二糖类化合物 25～33 的 ^{13}C-NMR 化学位移数据[6]①

C \ 化合物	25	26	27	28	29	30	31	32	33
1	94.9	98.9	104.2	95.0	94.9	93.9	93.7	94.5	97.3
2	73.1	76.8	74.0	71.4	71.8	71.1	71.3	72.6	75.6
3	74.2	77.4	75.7	70.2	74.9	70.8	73.7	72.7	75.6
4	81.7	81.5	79.8	77.8	77.4	75.4	74.8	70.5	70.5
5	74.2	77.4	75.7	72.2	76.1	71.9	74.8	72.7	77.2
6	63.0	63.1	61.3	61.6	61.6	61.1	61.1	67.2	62.2
1′	106.1	106.1	104.2	104.2	104.2	99.9	99.9	99.4	99.4
2′	73.9	73.9	72.2	72.2	72.2	72.7	72.7	70.5	70.5
3′	75.6	75.6	73.8	73.7	73.7	27.7	27.7	69.7	69.7
4′	71.5	71.5	69.8	69.8	69.8	69.4	69.4	70.4	70.4
5′	78.3	78.3	76.6	76.5	76.5	70.8	70.8		
6′	63.9	63.9	61.4	62.3	62.3	60.1	60.1	62.3	62.3

① 以 D_2O 为溶剂。

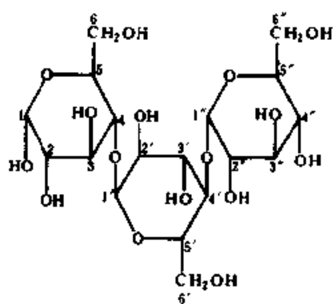


25. α-D-Glu 4－1β-D-Gal
26. β-D-Glu 4－1β-D-Gal
27. β-CH_3-D-Glu 4－1β-D-Gal
28. α-D-Man 4－1β-D-Gal
29. β-D-Man 4－1β-D-Gal
30. α-D-Man 4－1α-D-Glu
31. β-D-Man 4－1α-D-Glu
32. α-D-Glu 6－1α-D-Gal
33. β-D-Glu 6－1α-D-Gal

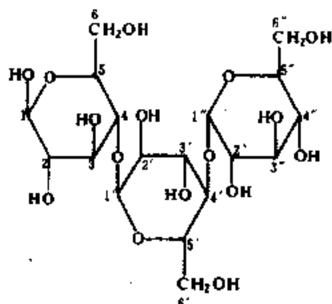
三、三糖的^{13}C-NMR化学位移

表 26-10　三糖 1～8 的^{13}C-NMR化学位移数据[2]

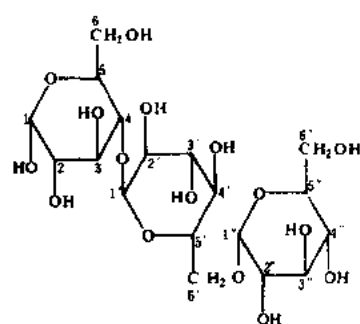
C \ 化合物	1	2	3	4	5	6	7	8
1	93.4	97.1	93.3	97.2	93.8	97.7	93.4	97.3
2	73.4	75.9	73.1	75.4	73.3	75.8	73.1	75.5
3	74.7	77.8	74.6	77.7	74.6	77.7	74.3	76.8
4	78.5	78.9	78.5	78.5	71.0	71.0	71.2	71.2
5	71.6	76.3	71.6	75.8	71.3	75.8	71.2	76.1
6	62.4	62.4	62.4	62.4	67.5	67.5	70.0	70.0
1′		101.1		101.1		99.3		103.7
2′		73.1		74.3		73.3		74.6
3′		74.7		74.6		74.6		77.1
4′		78.5		71.2		78.8		71.2
5′		72.7		71.2		71.6		76.1
6′		62.4		67.4		62.3		70.0
1″		101.1		99.3		101.1		103.7
2″		74.3		73.1		74.1		74.6
3″		75.1		74.6		75.0		77.1
4″		71.2		71.2		71.0		71.0
5″		73.4		73.1		73.0		77.1
6″		62.4		62.4		62.3		62.4



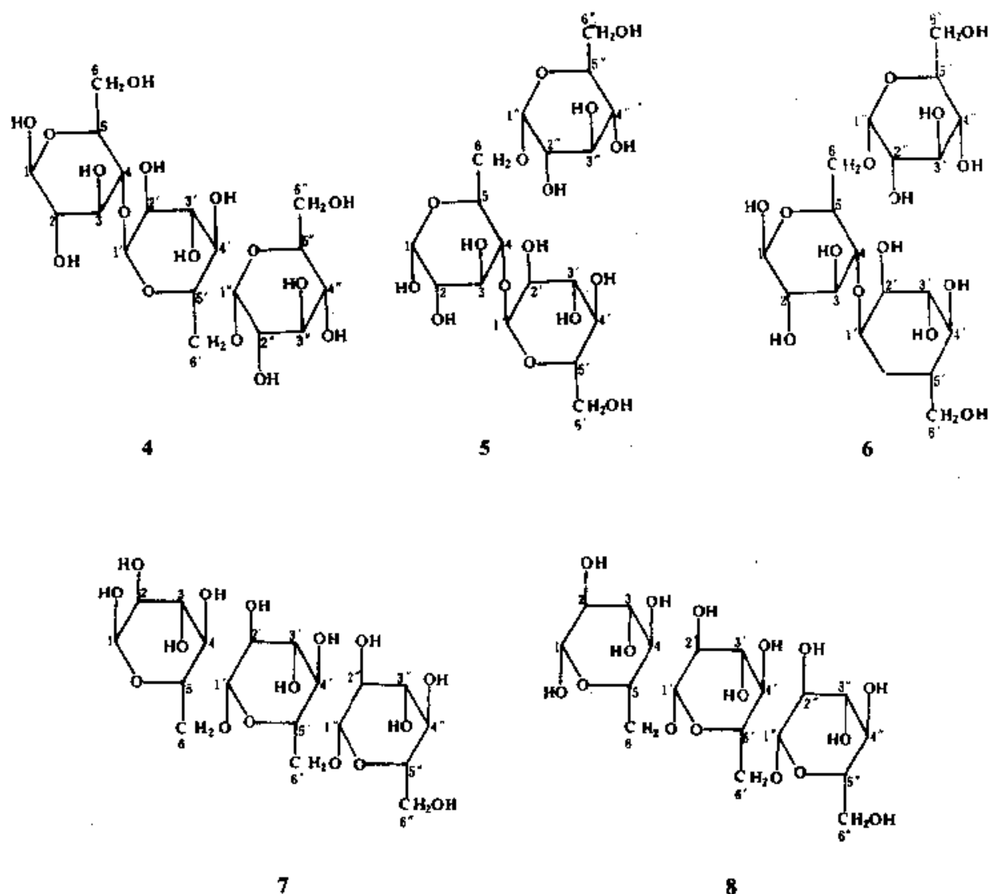
1



2



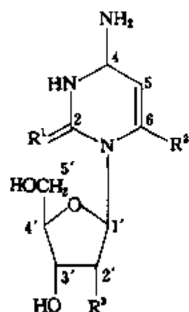
3



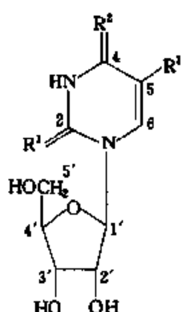
第二节　核苷及核苷酸的^{13}C-NMR 化学位移

表 26-11　胞嘧啶核苷、尿嘧啶核苷、胸腺嘧啶脱氧核苷及其衍生物 1～11 的^{13}C-NMR 化学位移数据[8]

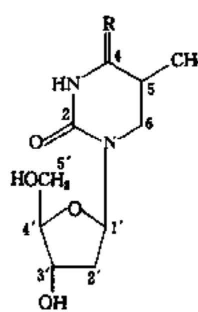
C \ 化合物	1	2	3	4	5	6	7	8	9	10	11
2	156.9	157.0	180.8	157.3	152.4	149.1	173.8	150.6	152.9	151.5	148.7
4	166.6	167.0	161.0	166.2	164.7	191.0	187.0	161.7	167.3	164.8	191.5
5	95.6	95.8	99.0	96.5	103.0	113.6	118.6	121.0	103.7	110.5	118.8
6	142.8	142.4	142.6	155.4	142.2	136.9	135.5	133.4	143.2	137.3	134.2
1′	90.1	86.5	94.4	92.9	89.1	89.6	94.3	88.6	89.6	85.0	85.8
2′	70.6	40.6	69.4	71.1	71.1	70.6	69.6	71.3	71.2	40.4	39.9
3′	75.1	71.8	76.0	71.8	74.8	74.9	75.6	74.2	75.1	71.6	71.2
4′	85.2	88.6	85.1	86.2	85.9	86.0	85.6	85.5	85.1	88.4	87.8
5′	61.8	62.6	60.8	63.2	62.2	61.7	60.6	62.4	64.6	62.4	62.1
其　他				20.8						13.2	17.8



1. $R^1 = O$, $R^2 = H$, $R^3 = OH$
2. $R^1 = O$, $R^2 = H$, $R^3 = H$
3. $R^1 = S$, $R^2 = H$, $R^3 = OH$
4. $R^1 = O$, $R^2 = CH_3$, $R^3 = OH$



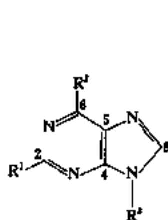
5. $R^1 = R^2 = O$, $R^3 = H$
6. $R^1 = O$, $R^2 = S$, $R^3 = H$
7. $R^1 = R^2 = S$, $R^3 = H$
8. $R^1 = R^2 = O$, $R^3 = OH$
9. $R^1 = R^2 = O$, $R^3 = OH_2PO_4$



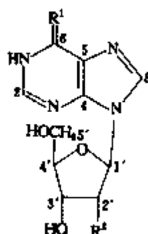
10. R = O
11. R = S

表 26-12 嘌呤、次黄苷、鸟苷、黄苷及其衍生物 12～22 的^{13}C-NMR 化学位移数据[8]

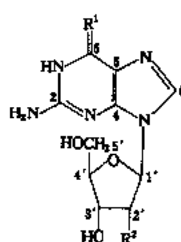
C \ 化合物	12	13	14	15	16	17	18	19	20	21	22
2	151.6	150.2	149.2	148.5	146.1	154.6	154.3	154.7	154.2	158.9	158.4
4	154.4	152.4	147.0	146.2	144.7	152.3	148.9	152.0	151.3	152.4	149.0
5	128.1	132.2	125.3	125.2	136.3	117.5	129.4	117.6	119.3	117.2	127.2
6	144.4	152.4	157.6	157.4	176.7	157.8	176.1	158.2	157.6	164.4	182.9
8	147.5	146.4	139.9	139.3	141.9	136.8	139.4	136.7	141.2	137.4	137.4
1′		89.4	88.8	84.4	88.4	87.2	87.9	83.8	88.9	89.8	89.9
2′		71.0	71.2	40.2	70.8	71.5	71.4	40.4	71.4	71.5	71.6
3′		75.0	75.2	71.4	75.1	74.8	76.0	71.8	74.8	74.8	75.0
4′		86.4	86.6	88.7	86.4	86.4	86.4	86.6	86.8	87.2	87.0
5′		61.7	62.3	62.2	62.0	62.2	62.4	62.8	62.5	62.2	62.2



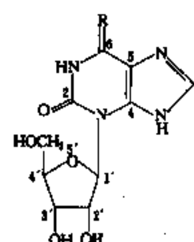
12. $R^1 = R^2 = R^3 = H$
13. $R^1 = H$, $R^2 = Cl$, $R^3 = \beta$-核糖基
20. $R^1 = Cl$, $R^2 = NH_2$, $R^3 = \beta$-核糖基



14. $R^1 = O$, $R^2 = OH$
15. $R^1 = O$, $R^2 = H_2$
16. $R^1 = S$, $R^2 = OH$



17. $R^1 = O$, $R^2 = OH$
18. $R^1 = S$, $R^2 = OH$
19. $R^1 = O$, $R^2 = H_2$



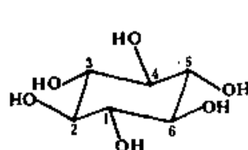
21. R = O
22. R = S

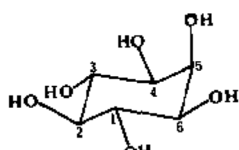
第三节　多元醇及氨基酸的^{13}C-NMR 化学位移

一、多元醇的^{13}C-NMR 化学位移

表 26-13　肌醇及其衍生物 1～10 的^{13}C-NMR 化学位移数据[7]

C \ 化合物	1	2	3	4	5	6	7	8	9	10
1	73.7	72.4	71.6	71.7	80.5	80.4	80.3	81.0	67.2	71.7
2	73.7	72.2	70.5	74.5	68.0	63.3	67.8	78.1	80.1	69.8
3	73.7	72.4	72.8	70.1	72.3	80.4	71.7	72.6	71.9	82.5
4	73.7	71.1	72.8	74.5	71.1	71.4	82.2	71.4	72.8	72.1
5	73.7	74.3	70.5	71.7	74.4	74.4	73.7	74.4	70.4	70.6
6	73.7	71.1	71.6	66.8	71.6	71.4	70.5	71.8	71.3	71.7
CH_3					56.9	57.4	59.7,56.7	61.5,57.4	56.8	59.4





1

2. —

5. D-1-O-CH_3

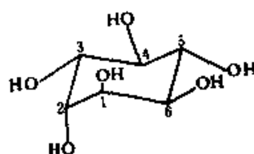
6. 1，3-O-CH_3

7. 1，4-O-CH_3

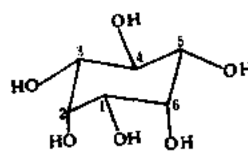
8. 1，2-O-CH_3

9. L-2-O-CH_3

10. D-2-O-CH_3

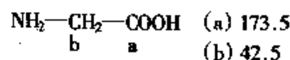


3

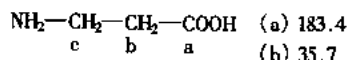


4

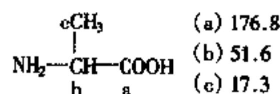
二、氨基酸的^{13}C-NMR 化学位移



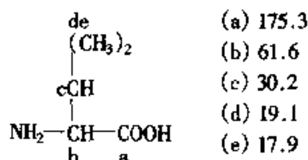
1



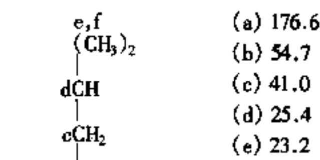
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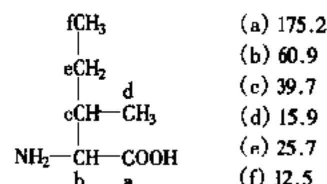
3



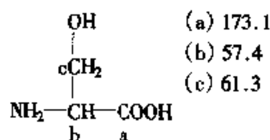
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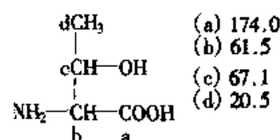
5



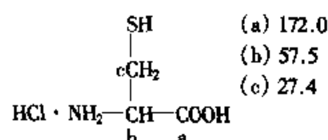
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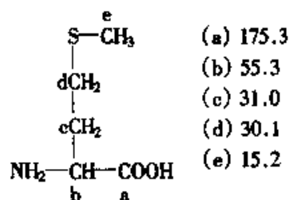
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8

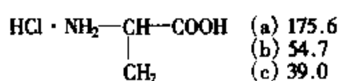


9



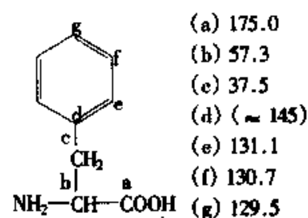
(a) 175.3
(b) 55.3
(c) 31.0
(d) 30.1
(e) 15.2

10



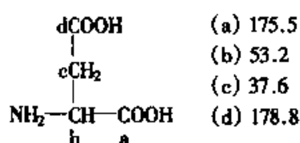
(a) 175.6
(b) 54.7
(c) 39.0

11



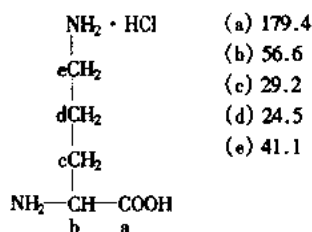
(a) 175.0
(b) 57.3
(c) 37.5
(d) (~ 145)
(e) 131.1
(f) 130.7
(g) 129.5

12



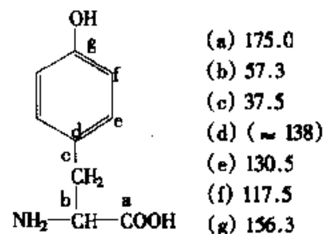
(a) 175.5
(b) 53.2
(c) 37.6
(d) 178.8

13



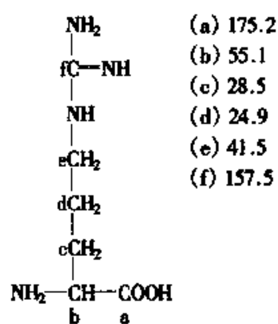
(a) 179.4
(b) 56.6
(c) 29.2
(d) 24.5
(e) 41.1

14



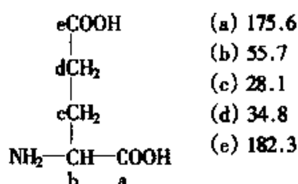
(a) 175.0
(b) 57.3
(c) 37.5
(d) (~ 138)
(e) 130.5
(f) 117.5
(g) 156.3

15



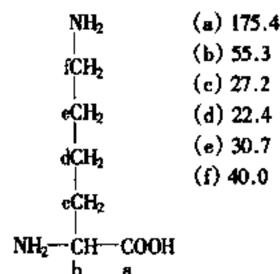
(a) 175.2
(b) 55.1
(c) 28.5
(d) 24.9
(e) 41.5
(f) 157.5

16



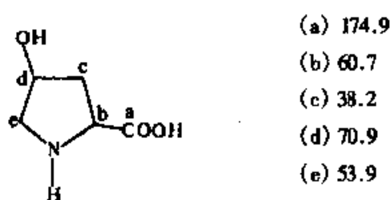
(a) 175.6
(b) 55.7
(c) 28.1
(d) 34.8
(e) 182.3

17



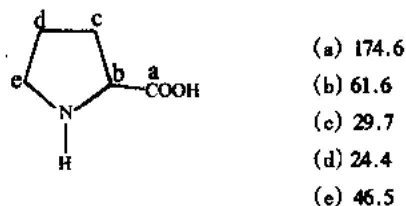
(a) 175.4
(b) 55.3
(c) 27.2
(d) 22.4
(e) 30.7
(f) 40.0

18



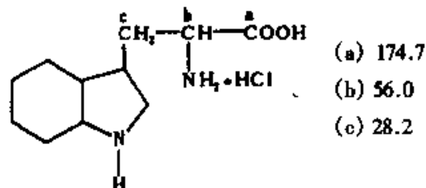
(a) 174.9
(b) 60.7
(c) 38.2
(d) 70.9
(e) 53.9

19



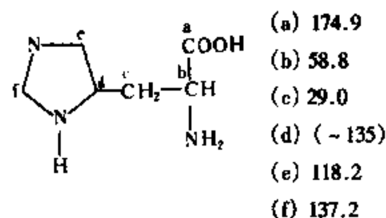
(a) 174.6
(b) 61.6
(c) 29.7
(d) 24.4
(e) 46.5

20



(a) 174.7
(b) 56.0
(c) 28.2

21



(a) 174.9
(b) 58.8
(c) 29.0
(d) (~ 135)
(e) 118.2
(f) 137.2

22

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第二十七章　偶合常数及常用溶剂的^{13}C-NMR化学位移图谱

第一节　碳-氢间的偶合常数

一、直接连接的^{13}C-^{1}H之间的偶合常数（$^{1}J_{C\text{-}H}$）

CH_4　125　CH_3Cl　151　$CH_2{=}CH_2$　156　△　161　◇134

159　HC≡CH 249　128　123　(a) 167　(b) 198

(a) 170 (b) 182　(a) 208 (b) 199　(a) 190 (b) 178　(a) 205　(a) 208　(a) 152 (b) 163 (c) 179

CH_3CH_3　125.0　CH_2F_2　184.5　HCO_2H　222.0　CH_3NH_2　133.0

CHF_3　239.1　HC≡N　269.0　CH_3OCH_3　140.0

CH_2O　172.0　$HC{\equiv}\overset{+}{N}H$　320.0　CH_3F　149.0　HCO_2^-　194.8

144　125.8　153　142.0　16.4　131.2

169　136.0　153.0　205　130.0

二、脂肪族化合物偶合常数计算的加和值（$^{1}J_{C\text{-}H}$）

$$J_{CHZ_1Z_2Z_3} = 125.0 + \sum_i Z_i$$

置　换　基	置换位置 Z_i	置　换　基	置换位置 Z_i	置　换　基	置换位置 Z_i
—H	0.0	—C≡CH	7.0	—NH_2	8.0
—CH_3	1.0	—C_6H_5	1.0	—$NHCH_3$	7.0
—$C(CH_3)_3$	-3.0	—F	24.0	—$N(CH_3)_2$	6.0
—CH_2Cl	3.0	—Cl	27.0	—$SOCH_3$	13.0
—CH_2Br	3.0	—Br	27.0	—CHO	2.0
—CH_2I	7.0	—I	26.0	—$COCH_3$	-1.0
—$CHCl_2$	6.0	—OH	18.0	—COOH	5.5
—CCl_3	9.0	—O—C_6H_5	18.0	—CN	11.0

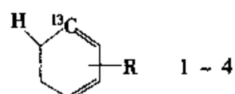
三、烷烃的远程^{13}C-^{1}H偶合常数

表 27-1 烷烃远程^{13}C-^{1}H偶合常数表

化合物	类型	J_{C-H}	化合物	类型	J_{C-H}
$H_3C—CH_3$	^2J	−4.5	H_a, O, H_b（环）	^2J_a ^3J_a ^2J_b	−2.9 +2.9 −4.4
$ClCH_2—CH_2Cl$	^2J	−3.4			
$CH_3CH_2CH_3$	^2J	−4.3			
$CH_3\cdots CH(OH)—CH_3$	^2J	0.7			
$CH_3—CH(X)—CH_3$	^2J	−4.0~4.7	S, H_a, H_b（环）	^2J_a ^2J_b ^3J_b	−4.1 −3.7 +4.2
$CH_3—CH(X)—CH_3$	^2J	4.6~5.8			

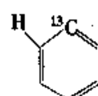
四、2个键间的碳氢偶合常数（$^2J_{C-H}$）

$H—C—{}^{13}C—$	1~6	$H—CH_2—{}^{13}CH_3$	4.5
$H—C{=}{}^{13}C—$	0~16	$H—CH{=}{}^{13}CH_2$	2.4
$H—C{\equiv}{}^{13}C—$	40~60	$H—CCl{=}{}^{13}CHCl$	16.0
$H—C—{}^{13}CO—$	5~8	$H—C{\equiv}{}^{13}CH$	49.3
$H—CO—{}^{13}C—$	20~50	$H—CH_2—{}^{13}CO—CH_3$	5.5
		$H—CO—{}^{13}CH_3$	26.7



1~4

R为任意取代基



1.0

五、取代烯烃^{13}C-^{1}H的偶合常数

表 27-2 取代烯烃^{13}C-^{1}H偶合常数表

化合物	$^1J_{C-H}$	$^2J_{C-H}$	$^3J_{C-H}$	化合物	$^1J_{C-H}$	$^2J_{C-H}$
$H_2C{=}CH_2$	156.4	(−) 2.4		$H_\alpha(Cl)C{=}CH_\beta H_\gamma$	198	β (+) 7.5 γ (−) 7.9
$H_2C{=}C{=}CH_2$	167.8	3.9	7.7	$H_\alpha(Cl)C{=}CH_\beta H_\gamma$	162	α (+) 6.9
S, S（环）	179.8	8.1		$HClC{=}CClH$（反式）		(+) 0.8
$H_2C{=}CHF$	159.1			$HClC{=}CClH$（顺式）		(+) 16.0
$H_2C{=}CHF$	200.2			$(CH_3)_2C$, $CH{=}CH$（环）	221	
$HIC{=}CIH$	194.2	(−) 1.4		H（环丙烯）	228.2	

续表

化合物	$^1J_{C\text{-}H}$	$^2J_{C\text{-}H}$	$^3J_{C\text{-}H}$	化合物	$^1J_{C\text{-}H}$	$^2J_{C\text{-}H}$
I(H)C=C(H)I	187.9	11.0		环丁烯（C—H）	170	
亚环己基=C$H_c$$H_t$				H_α(H$_\beta$)C=C(H_γ)—C(=O)H	α = 162.3 β = 156.6	
			(H_c) 6.4 (H_t) 11.4	H_α(H$_\beta$)C=C(H_γ)—C(=O)H	γ = 162.3	

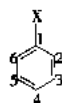
六、炔烃^{13}C-^{1}H 的偶合常数

化合物	$^1J_{C\text{-}H}$	$^2J_{C\text{-}H}$	$^3J_{C\text{-}H}$
H—C≡CH	249	49.3	
$\overset{3}{C}\overset{3}{H_3}$—$\overset{2}{C}$≡$\overset{1}{C}$—$\overset{1}{H}$		50.8 (C_2—H_1)	−10.6 (C_1—H_3)
$\overset{2}{H}$($\underset{1}{H}$)$\overset{1}{C}$=$\overset{2}{C}$($\underset{3}{H}$)—$\overset{3}{C}$≡$\overset{4}{C}$—$\overset{4}{H}$	251.7 (C_4—H_4)	50.2 (C_3—H_4) 2.0 (C_3—H_3)	4.0 (C—H_3) 16.3 (C_3—H_1) 9.5 (C_3—H_2)

七、环烯类和芳香化合物的^{13}C-^{1}H 偶合常数

化合物	$^1J_{C\text{-}H}$	化合物	$^1J_{C\text{-}H}$
环丙烯（=C—H）	228.2	苯（C—H）	157.7
环丁烯（=C—H）	170	环辛烯（=C—H）	156.2
环戊烯（=C—H）	161.6	薁（C$_6$—H）	154
薁（C$_1$—H，C$_2$—H）	164，179	环庚烯（=C—H）	156.0
环己烯（=C—H）	158.4	草鎓离子（C—H）	166.8 ($^3J_{C\text{-}H}$ = 9.99)

八、单取代苯类的^{13}C-^{1}H 偶合常数



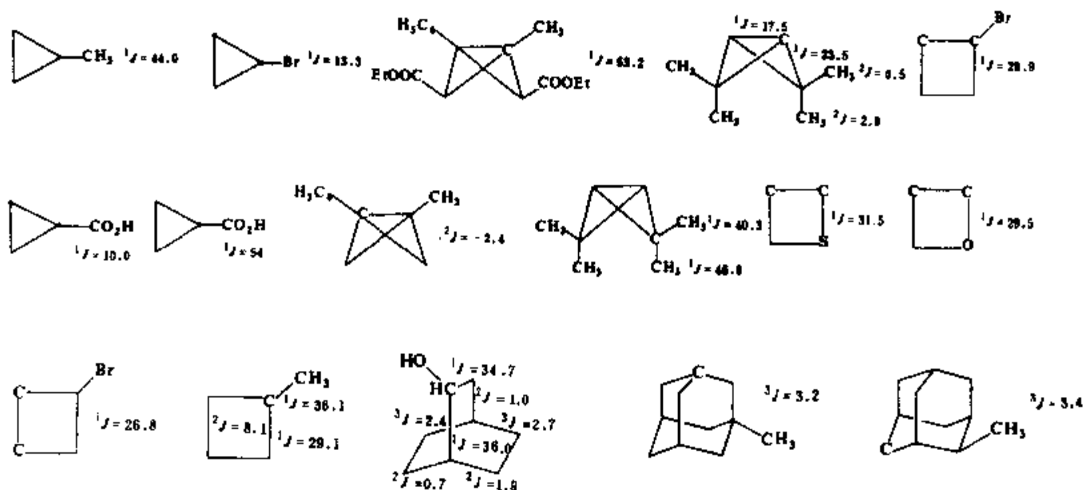
X	$^{2}J_{12}$	$^{3}J_{13}$	$^{4}J_{14}$	$^{1}J_{22}$	$^{3}J_{26}$	$^{3}J_{35}$
F	−4.89	10.95	−1.73	162.55	4.11	9.02
NO_2	−3.57	9.67	−1.75	168.12	4.45	8.18
OCH_3	−2.79	9.22	−1.51	158.52	4.80	8.73
CHO	0.29	7.19	−1.26	160.95	6.25	7.58
CH_3	0.54	7.61	−1.40	155.89	6.59	7.91
Si $(CH_3)_3$	4.19	6.34	−1.10	156.14	8.63	7.26

第二节　^{13}C-^{13}C、^{13}C-^{19}F、^{31}P-^{13}C 间的偶合常数及含磷化合物的^{13}C-NMR 化学位移

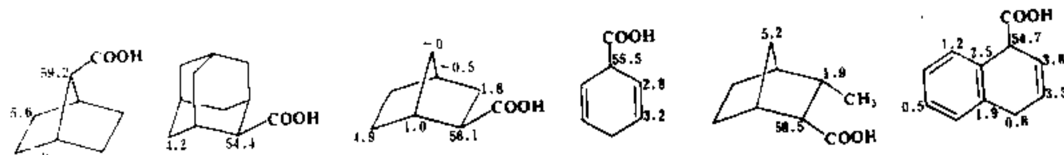
一、^{13}C-^{13}C 间的偶合常数

1. 烷烃及其衍生物^{13}C-^{13}C 间的偶合常数（$J_{C\text{-}C}$）

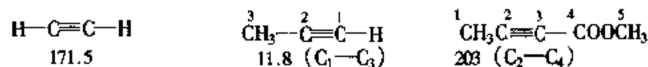




2. 羧酸的^{13}C-^{13}C 偶合常数



3. 炔烃^{13}C-^{13}C 偶合常数（Hz）



二、^{13}C-^{19}F 间的偶合常数

F—CH₂—CH₂—CH₂—CH₂—C₄H₉ ($F-CH_2-CH_2-CH_2-CH_2-C_4H_9$)

	J
CH_2	164.8
CH_2	18.3
CH_2	6.2
CH_2	~0

CF_3—COOH

	J
CF_3	294
COOH	46

Fluorocyclohexane (F at a; b, c, d):

	J
(a)	171
(b)	19
(c)	5
(d)	0

Fluorobenzene (F at a; b, c, d):

	J
(a)	245
(b)	21
(c)	8
(d)	3

$C_6H_5CF_3$ (CF_3 at b; c, d, e):

	J
(a)	271.7
(b)	32.3
(c)	3.9
(d)	1.3
(e)	~0

2-Fluoropyridine (F at a; b, c, d, e):

	J
(a)	236.3
(b)	37.6
(c)	7.5
(d)	4.2
(e)	14.9

3-Fluoropyridine (F at b; a, c, d, e):

	J
(a)	22.6
(b)	255.1
(c)	17.7
(d)	3.7
(e)	3.7

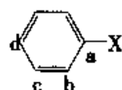
4-Fluoropyridine (F at c; a, b):

	J
(a)	6.4
(b)	16.1
(c)	261.8

三、含磷化合物的^{13}C-NMR 化学位移和^{31}P-^{13}C 间的偶合常数



取代基 X	X—CH₂—		—CH₂—		—CH₂—		CH₃	
	δ	J	δ	J	δ	J	δ	J
$-PCl_2$	42.9	44	25.1	14	23.4	11	13.7	0
$-P(n\text{-}C_4H_9)_2$	28.6	14	27.9	15	24.8	10	14.0	0
$-P^+(n\text{-}C_4H_9)_3$	18.7		23.7		24.1		13.3	
$-PO(n\text{-}C_4H_9)_2$	27.8	66	24.0	5	24.4	13	13.6	0
$-PS(n\text{-}C_4H_9)_2$	30.9	51	24.6	4	24.0	16	13.6	0
$-OP(O-n\text{-}C_4H_9)_2$	61.9	11	33.4	5	19.1	0	13.7	0
$-OPO(O-n\text{-}C_4H_9)_2$	67.2	6	32.6	7	18.9	0	13.6	0



取代基 X	a		b		c		d	
	δ	J	δ	J	δ	J	δ	J
$-P(C_6H_5)_2$	137.2	12	133.6	20	128.4	7	128.5	0
$-O-P(O-C_6H_5)_2$	151.1	4	124.1	7	129.5	0	124.1	0
$-O-PO(O-C_6H_5)_2$	150.4	8	120.1	5	129.7	0	125.5	0

第三节　常用溶剂的^{13}C-NMR 化学位移图谱

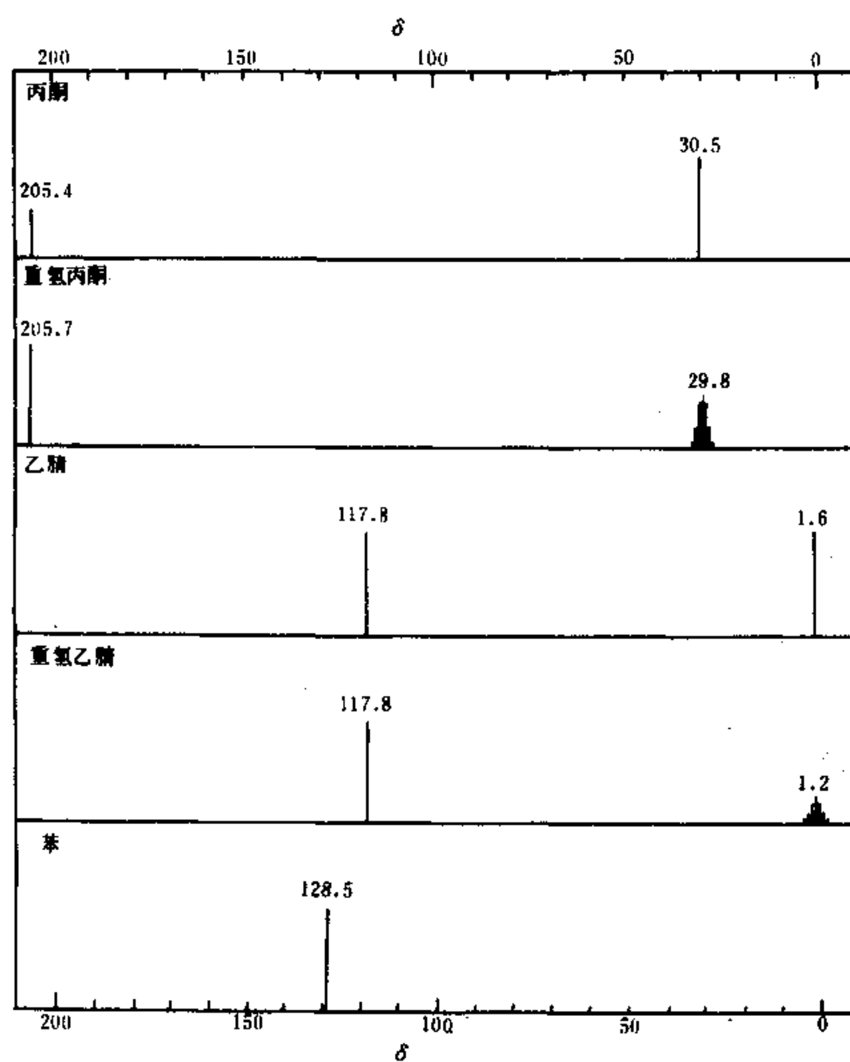


图 27-1　丙酮、重氢丙酮、乙腈、重氢乙腈、苯的^{13}C-NMR 化学位移图谱

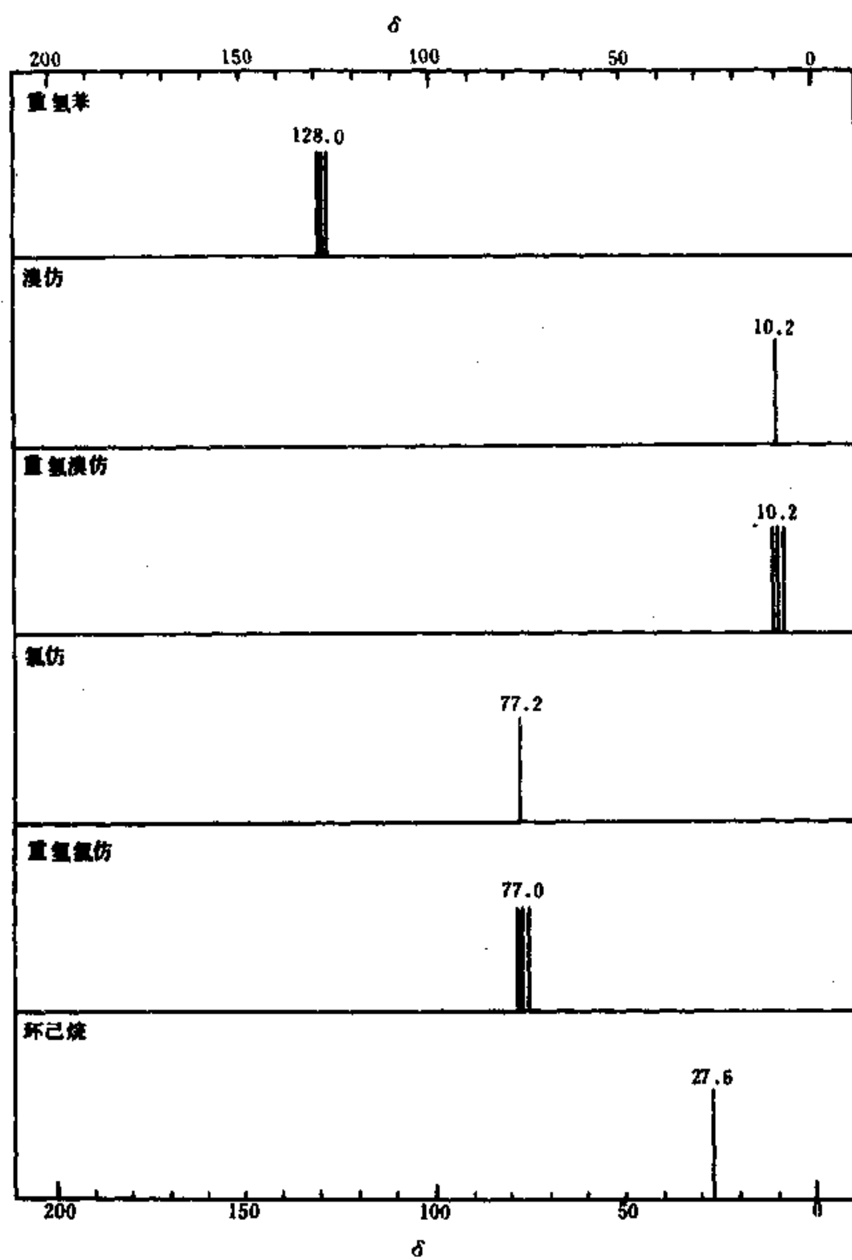


图 27-2 重氢苯、溴仿、重氢溴仿、氯仿、重氢氯仿、环己烷的^{13}C-NMR 化学位移图谱

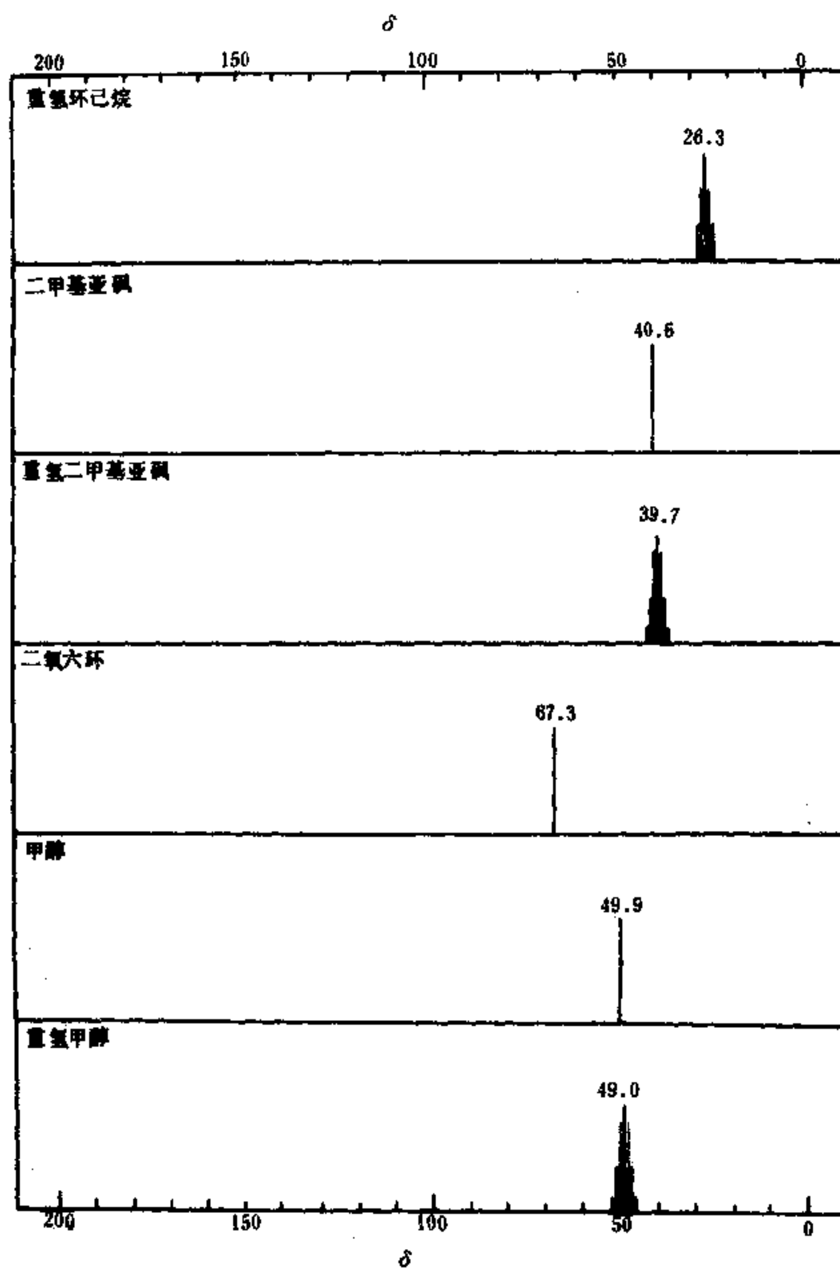


图 27-3 重氢环己烷、二甲基亚砜、重氢二甲基亚砜、二氧六环、甲醇、重氢甲醇的^{13}C-NMR 化学位移图谱

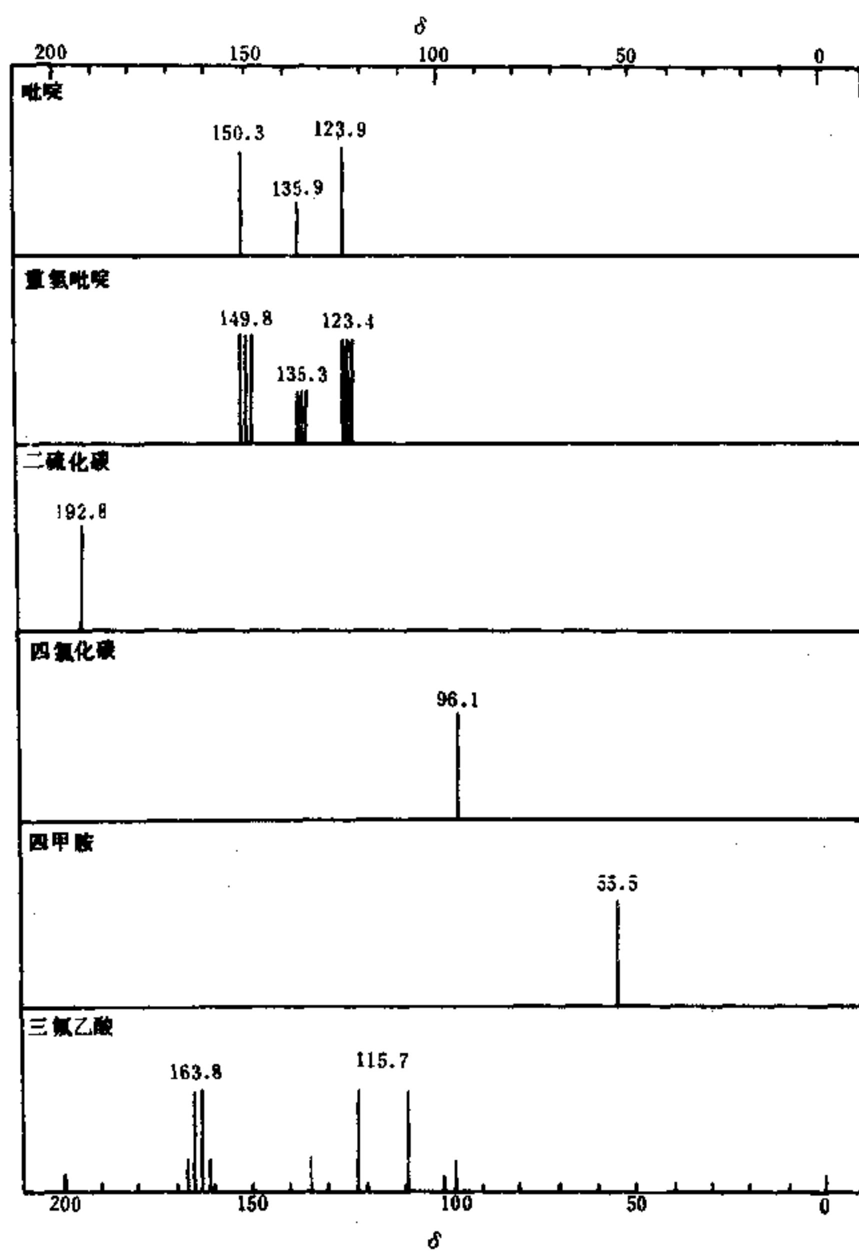


图 27-4 吡啶、重氢吡啶、二硫化碳、四氯化碳、四甲胺、三氟乙酸的 ^{13}C-NMR 化学位移图谱

附　　录

一、NMR谱中一些重要原子核的性质表

原子核	天然丰度/%	相对灵敏度	自旋量子数	不同磁场下的拉摩频率/MHz				
				$H_0=4.7T$	$H_0=7.05T$	$H_0=9.4T$	$H_0=11.75T$	$H_0=14.1T$
^{1}H	99.985	1.00	1/2	200.00	300.00	400.00	500.00	600.00
^{2}H	0.015	9.65×10^{-3}	1	30.70	46.05	61.40	76.75	92.10
^{7}Li	92.58	0.294	3/2	77.72	116.59	155.45	194.31	233.16
^{9}Be	100	1.39×10^{-2}	-3/2	28.11	42.16	56.21	70.27	84.32
^{10}B	19.58	1.99×10^{-2}	3	21.49	32.24	42.99	53.73	64.48
^{11}B	80.42	0.165	3/2	64.17	96.25	128.34	160.42	192.50
^{13}C	1.108	1.59×10^{-2}	1/2	50.29	75.44	100.59	125.73	150.88
^{14}N	99.63	1.01×10^{-3}	1	14.45	21.67	28.90	36.12	43.34
^{15}N	0.37	1.04×10^{-3}	-1/2	20.27	30.40	40.53	50.66	60.80
^{17}O	3.7×10^{-2}	2.91×10^{-2}	-5/2	27.11	40.67	54.23	67.78	81.34
^{19}F	100	0.833	1/2	188.15	282.23	376.31	470.38	564.46
^{23}Na	100	9.25×10^{-2}	3/2	52.90	79.35	105.81	132.26	158.71
^{27}Al	100	0.260	5/2	52.11	78.17	104.23	130.28	156.34
^{29}Si	4.70	7.84×10^{-3}	-1/2	39.73	56.60	79.46	99.32	119.19
^{31}P	100	6.63×10^{-2}	1/2	80.96	121.44	161.92	202.40	242.88
^{33}S	0.76	2.26×10^{-3}	3/2	15.34	23.01	30.68	38.35	46.02
^{35}Cl	75.53	4.7×10^{-3}	3/2	19.60	29.40	39.19	48.99	58.79
^{39}K	93.10	5.08×10^{-4}	3/2	9.33	14.00	18.67	23.33	28.00
^{51}V	99.76	0.382	7/2	52.56	78.85	105.13	131.41	157.69
^{55}Mn	100	0.178	5/2	49.33	73.99	98.66	123.32	147.98
^{57}Fe	2.19	3.38×10^{-5}	1/2	6.46	9.69	12.93	16.16	19.39
^{59}Co	100	0.281	7/2	47.23	70.84	94.46	118.07	141.68
^{65}Cu	30.91	1.14	3/2	56.79	85.18	113.58	141.97	170.36
^{75}As	100	2.51×10^{-2}	3/2	34.25	51.38	68.51	85.63	102.76
^{77}Se	7.58	6.93×10^{-3}	1/2	38.13	57.20	76.27	95.33	114.40
^{79}Br	50.54	7.86×10^{-2}	3/2	50.11	75.16	100.22	125.27	150.32
^{87}Rb	27.85	0.175	3/2	65.44	98.16	130.88	163.60	196.32
^{93}Nb	100	0.482	9/2	48.89	73.33	97.77	122.22	146.66
^{103}Rh	100	3.12×10^{-5}	-1/2	6.29	9.44	12.59	15.74	18.88
^{113}Cd	12.26	1.09×10^{-2}	-1/2	44.37	66.55	88.74	110.92	133.10
^{119}Sn	7.61	5.18×10^{-2}	-1/2	74.54	111.82	149.09	186.36	223.63
^{121}Sb	57.25	0.160	5/2	47.86	71.79	95.73	119.66	143.59
^{127}I	100	9.34×10^{-2}	5/2	40.01	60.02	80.03	100.04	120.04
^{133}Cs	100	4.74×10^{-2}	7/2	26.23	39.35	52.47	65.58	78.70
^{183}W	14.40	6.98×10^{-5}	1/2	8.32	12.48	16.64	20.80	24.97
^{195}Pt	33.80	9.94×10^{-3}	1/2	43.00	64.49	85.99	107.49	128.99
^{199}Hg	16.84	5.67×10^{-3}	1/2	35.65	53.48	71.31	89.14	106.96
^{201}Hg	13.22	1.42×10^{-3}	-3/2	13.20	19.80	26.40	33.00	39.60
^{205}Tl	70.50	0.192	1/2	115.37	173.05	230.73	288.42	346.10
^{207}Pb	22.6	9.13×10^{-3}	1/2	41.84	62.77	83.69	104.61	125.53

二、重要NMR专用名词缩写英汉对照表

ADA（altercnated delayed acquisition）交替延迟采集数据法

ADC（analog to digital converter）模数转换器

Anti-反式（邻位碳取代基的反式）

APFG（alternating pulsed field gradient）交变脉冲场梯度

APIR（alternate phase inversion recovery）交替相位反转恢复

APS（aperiodic pulse sequence）非周期脉冲序列

AQ（acquision time）取数时间

BIRD（bilinear rotation deccoupling）双线性旋转去偶

CIDEP（chemically induced dynamic electron polarization）化学诱导动态电子极化

CIDNP（chemically induced dynamic nuclear polarization）化学诱导动态核极化

CMR ^{13}C-NMR的缩写

COLOC（correlation spectroscopy via long range couplings）碳氢远程偶合相关谱

COMPUL（composite pulse）组合脉冲

COSY（correlated spectroscopy）二维化学位移相关谱

CPMAS（cross polarization and magic angle spinning）交叉极化和魔角旋转

CSA（chemical shift anisotropy）化学位移各向异性

CT（computed tomography）计算机断层成像

CW（continuous wave）连续波

DAC，D/A（digital to analog converter）数模转换器

2D-FT NMR（two-dimensional FT NMR）二维傅里叶变换核磁共振

DANTE（delays alternating with nutation for transient excitation）一种选择性激发脉冲序列，用以抑制溶剂信号

DD [dipole-dipole interaction or relaxation mechanism] 偶极-偶极相互作用或弛豫机制

DEPT（distortionless enhancement by polarization transfer）无畸变极化转移增益

DFT（delay Fourier transformation）延迟傅里叶变换

DISCO（difference and sums in COSY spectra）COSY谱的差与和

DNMR（dyanmic NMR）动态核磁共振

DNP（dynamic nuclear polarization）动态核极化

DOE（dynamic Overhauser effect）动态欧沃豪斯效应

DQ（double-quantum）双量子

DQC（double-quantum coherence）双量子相干

DQD（digital quadrature detection）数字正交检测

DQF（double quantum filter）双量子滤波

DR（digital resolution）数字分辨率

DSC（4，4-dimethyl 4-silapentane sodium carboxylate）4，4-二甲基4-硅戊烷羧酸钠（用作^{1}HNMR参考标准物）

DSS（4，4-dimethyl 4-silapentance sodium sulfonate）4，4-二甲基4-硅戊烷磺酸钠盐（用作^{1}HNMR参考标准物）

E-COSY（exclusive COSY）专用COSY谱

EFG（electric field gradient）电场梯度

ELDOR（electron-electron double resonance）电子-电子双共振

ENDOR（electron-nuclear double resonance）电子-核双共振

EXSY（exchange spectroscopy）交换相关谱

FID（free induction decay）自由感应衰减

FFT（fast Fourier transform）快速傅里叶变换

FOCSY（foldover corrected spectroscopy）折叠校正谱

FT（Fourier transform）傅里叶变换

FW (filter width) 滤波宽度
HDQC (heteronuclear double quantum correlation) 异核双量子相关
HEHAHA (heteronuclear Hartmann Hahn spectroscopy) 异核 Hartmann Hahn 谱
HET2DJ (heteronuclear two-dimensional J-spectroscopy) 异核二维 J 相关谱
HETCOR (heteronuclear correlation) 异核相关
HMDS (hexamethyldisilane) 六甲基二硅烷 (质子参考标准物)
HMDSA (hexamethyldisilazane) 六甲基二硅氮烷 (质子参考标准物)
HMDSO (hexamethyldisiloxane) 六甲基二硅醚 (质子参考标准物)
HOESY (heteronuclear NOE spectroscopy) 异核 NOE 谱
HOHAHA (homonuclear Hartmann-Hahn spectroscopy) 同核 Hartmann-Hahn 谱
HOMCOR (homonuclear correlated spectroscopy) 同核相关谱
HOMO (highest occupied molecular orbital) 最高占据的分子轨迹
HR (high resolution) 高分辨
HS (homogeneity-spoiling) 匀场破坏
HSP (homogeneity-spoiling pulse) 匀场破坏脉冲
HSQC (heteronuclear single quantum coherence) 异核单量子相干
HTD (heteronuclear decoupling) 异核去偶
ICE (indirect connectivity experiment) 间接关联实验
IHO (internal homonuclear lock) 同核内锁
INDOR (internuclear double resonance) 核间双共振
INEPT (insensitive nuclei enhanced by polarization transfer) 非敏核极化转移增益
INEPTR (refocused INEPT) 重聚 INEPT
I/O (input/output) 输入输出, 输入输出设备
IRFT (inversion-recovery Fourier transform) 反转回复傅里叶变换 (一种测量 T_1 的实验方法)
IRSE (inversion-recovery spin echo) 反转回复自由回旋
JCP (J cross-polarization) J 交叉极化
JMOD (J-modulated spin-echo) J 调制自旋回波
JR (jump and return sequence) 跳跃和回复序列
JRES2D (J-resolved 2-dimensional spectroscopy) J 分解二维谱
LB (line broadening) 谱线加宽
LC-NMR (liquid chromatography-NMR) 液相色谱核磁共振
LIS (lanthanide-induced shift) 镧化物诱导位移
LP (linear prediction) 线性预测
LPCS (light pen control system) 光笔控制系统
LSR (lanthanide shift reagent) 镧化物位移试剂
MAR (magic-angle rotation) 魔角旋转
MAS (magic spinning) 魔角旋转
MCCP (multiple contact cross polarization) 多次接触交叉极化
MFE (multiple-frequency excitation) 多频率激发
MIONP (microwave-induced optical nuclear polarization) 微波诱导光效应核极化
MLEV (composite pulse decoupling sequence) 复合脉冲去偶序列
MQC (multiple quantum coherences) 多量子相干
MQ-COSY (multiple quantum correlated spectroscopy) 多量子相关谱
MQF-COSY (multiple quantum filter correlated spectroscopy) 多量子滤波相关谱
MQT (multiple quantum transition) 多量子跃迁
MQTSY (multiple-quantum transition spectroscopy) 多量子跃迁谱
MRI (nuclear magnetic resonance imaging) 核磁共振成像

MW（microwave）微波

NMR（nuclear magnetic resonance）核磁共振

NMR-CT（NMR computed tomography）核磁共振计算机断层成像

NMR-I（NMR imaging）核磁共振成像

NOE（unclear Overhauser effect）核欧沃豪斯效应

NOESY（nuclear Overhaser effect spectroscopy）二维 NOE 谱

NORD（noise-modulated off-resonance decoupling）噪音调制偏共振去偶

NORSE（noise off-resonance spin echo）噪音偏共振自旋回波

NQC（nuclear quadrupole coupling）核四极偶合

NQCC（nuclear quadrupole coupling constant）核四极偶合常数

NQR（nuclear quadrupole resonance）核四极共振

ONP（optical nuclear polarization）光效应核极化

PAPS（phase alternating pulse sequence）相位交替脉冲序列

PARR（paramagnetic relaxation reagent）顺磁弛豫试剂

PAS（pulse-alternated sequence）交替脉冲序列

PCS（pseudo-contact shift）假接触位移

PD（pulse delay）脉冲延迟

PFG（pulsed field gradient）脉冲场梯度

PFP（pulsed free precession）脉冲自由进动

PFT（pulse Fourier transform）脉冲傅里叶变换

PHD（pulsed homonuclear decoupling）脉冲同核去偶

PMR（proton magnetic resonance）质子磁共振

PRE（proton relaxation enhancement）质子弛豫增益

PRFT（partialy relaxed FT）部分弛豫傅里叶变换

PS［progressive saturation（90°-τ-90°）］逐渐饱和法

PSD（phase sensitive detector）相敏检波器

PSFT（progressive saturation Fourier transfrom）逐渐饱和傅里叶变换法

PT（polarization transfer）极化转移

PTR（refocused polarization transfer）重聚极化转移

QCC（quadrupole coupling constant）四极偶合常数

QF（quadrupole moment/field gradient）四极矩/场梯度

QP（standard quadrature phase cycle）标准正交相位循环

QPD（quadrature phase detection）正交相位检测

QSEX（quadrature seletive excitation）正交选择激发

QUAD（quadrupole echo）四极回波

RAM（random access memory）随机存取存储器

RCOSY（relayed coherence transfer spectroscopy）接力相干转移谱

RCT（relayed coherence transfer）接力相干转移

Relay COSY（relayed correlation spectroscopy）接力相关谱

Rf（radio frequency）射频

RJCP（refocused JCP）重聚 JCP（一种交叉极化实验）

ROESY（rotating-frame Overhauser enhancement spectroscopy）旋转框架欧沃豪斯增益谱

ROM（read-only memory）只读存贮器

ROTO（ROESY transfer followed by TOCSY transfer）二种脉冲序列组合

RSFT（rapid-scan Fourier transform）快扫傅里叶变换

SC（scalar）标量

SCM（superconducting magnet）超导磁体

SDEPT（selective DEPT）选择性 DEPT 法

SE（spin-echo）自旋回波

SECSY（spine-echo correlated spectroscopy）自旋-回波相关谱

SEDOR（spin-echo double resonance）自旋回波双共振

SEFT（spin-echo Fourier transform）自旋回波傅里叶变换

SELINCOR（selective inverse detection of C, H correlation）选择性碳氢关联反转检测法

SEMQT（spin-echo multiple-quantum spectrum）自旋回波多量子谱

SEPT（selective INEPT）选择性 INEPT

SFORD（single frequency off-resonance decoupling）单频率偏共振去偶

SHECOR（selective heteronuclear correlation）选择性异核相关

SHFS（super hyperfine structure）超精细结构

SI（memory size）内存容量

SIMBA（selective inverse multiple-bond analysis）选择性反转多键（远程）分析

SIS（substituent-induced shift）取代基诱导位移

S/N（signal/noise）信噪比

SPD（single phase detection）单相检测

SPE（singe pulse excitation）单脉冲激发

SPI（selective population inversion）选择性布居反转

SPT（selective population transfer）选择性布居转移

SQ（sing-quantum）单量子

SRFT（saturation recovery Fourier transform）饱和回复傅里叶变换（测量弛豫时间）

SSBF（single side-band filter）单边带滤波

SW（spectral window）谱图窗口

SWR（spin wave resonance）自旋波共振

Syn-顺式（指邻位碳取代基的顺式）

T（Tesla）特斯拉（磁感应单位或磁通量单位等于一平方米-韦伯）

τ_c（correlation time）相关时间

TANGO（testing for adjacent nuclei with gyration operator）一种脉冲序列用于测量 C-H 远程偶合

TMS（tetramethylsilane）四甲基硅烷

TOCSY（total correlation spectroscopy）全相关谱

TOE（truncated driven nuclear Overhauser enhancement）截断驱动核欧沃豪斯增益

TORO（TOCSY transfer followed by ROESY transfer）二种脉冲序列组合

TOSS（total suppression of side band）边带峰全抑制

TS（time-sharing procedures）时间均分过程

VNAFT（method of variable nutation angle）一种测量弛豫时间 T_1 的实验方法

VT（variable temperature）变温

WAHUHA［Waugh, Huber and Haeberlen cycle of pulses］一种用于固体高分辨的多脉冲序列

WALTZ（wideband alternating phase low-power technique for zero residue splitting）^{13}C 宽带去偶脉冲序列

WEFT（water-eliminated FT）去水峰傅里叶变换

ZQC（zero quantum coherence）零量子相干

三、本书中其他缩写符号表

Ac	乙酰基
allo	阿洛糖基
altro	阿卓糖基
Ang	当归酰基
anti	反
api	芹菜糖基
Ar	芳基
ara	阿拉伯糖基
Arafur	阿糖呋喃型
Arapy	阿糖吡喃型
ax	直立键
bd	宽双重峰
br，b	宽峰
Bz	苯甲酰
bs	宽单峰
n-Bu	正丁基
i-Bu	异丁基
t-Bu	叔丁基
Bz	苄基
cis	顺式
cou、ctyl	香豆酰基
Cin	肉桂酰
d（doublet）	双重峰
dd	2个双重峰
ddd	3个双重峰
dl	外消旋
dt	2个三重峰
endo	内型
eq	平伏键
erythro	赤藓糖基
Et	乙基
exo	外型
gem	偕
Glu、glu	葡萄糖基
lip	酯基
m	间
m	多重峰
manno	甘露糖基
Me	甲基
meso	内消旋
o	邻
octet	八重峰
o（overlapping）	重叠（峰）
oxo	氧代
p	对
Ph	苯基
Pm	3-甲基-2-丁烯基
Pro	丙基
i-pro	异丙基
q（quartet）	四重峰
qui（quintet）	五重峰
qq	2个四重峰
R	烷基
Rha、rha	鼠李糖基
ribose	核糖基
s（singlet）	单峰
sxt（sextet）	六重峰
sep（septet）	七重峰
sinapoyl	芥子酰基
syn	顺
t（triplet）	三重峰
trans	反式
Trop	托品酰基
Ts	对甲苯磺酰基
i-Val	异戊酰基
vic	邻位
Xyl、xyl	木糖基

索　　引

一画

二画

三画

四画

五画

六画

七画

八画

九画

十画

十一画

十二画

十三画

十四画以上